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PAPERS ACCEPTED FOR PUBLICATION:

On a Balance to be Used in Elementary Chemistry. By C. E. Linebarger.
The Action of Organic Acids upon Nitrils. By J. A. Mathews.
The Action of Metallic Thiocyanides upon Aliphatic Chlorhydrins. By W. D. Engle.
Notes on Taka-diastase. By W. E. Stone and H. E. Wright.
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THE ATOMIC MASS AND DERIVATIVES OF SELENIUM.[1]

BY VICTOR LENHER.

Received June 6, 1898.

INTRODUCTION.

THE following contribution to our knowledge of selenium was undertaken with the view of studying the various derivatives and reactions of the element, and using such methods or compounds as would prove available in the determination of its atomic mass.

In the series presented, ratios have been determined in compounds differing widely in character and composition, and by methods entirely unlike in nature.

The action of hydrochloric acid gas upon the salts of acid oxides which possess the power of forming volatile compounds with it, affords a clean and accurate method, which can be used in establishing the atomic ratio.

A salt of such a character, when subjected to the action of the gas, yields a substance removed at once from the field of action, while in the vessel which contained the original salt there remains a chloride which can be directly weighed.

Such a method almost completely eliminates the factor of personal error, in that the operator needs but weigh the original

[1] Author's thesis for the Degree of Doctor of Philosophy.

salt and the resulting chloride, no manipulation intervening in which he is directly concerned.

If it be possible to use a salt whose resulting chloride can be directly reduced to metal, we have a means of establishing from one salt two series of ratios, which if agreeing, both as individuals and series, means that a ratio has been established comparable to that existing between the metal and its chloride. If two such series agree, a direct proof is established of the purity of material and accuracy of the method.

An ideal salt for such treatment is a salt of silver; first, since its chloride can be directly reduced to metal by heating in a current of hydrogen gas; second, the ratio between silver and chlorine is one of the most firmly established ratios. Silver selenite is an anhydrous salt, which crystallizes well, is unaffected by light, and is perfectly stable. This substance, when treated with gaseous hydrochloric acid, yields silver chloride and a hydroxychloride of selenium, corresponding in composition and properties to that obtained by A. Ditte,[1] when acting on selenium dioxide with hydrochloric acid gas.

In the first series of experiments, silver selenite was weighed, treated with hydrochloric acid gas, and silver chloride formed, which was weighed. In the second series, silver selenite was weighed, converted into silver chloride, which was weighed, the chloride was reduced in hydrogen to metal, and this again weighed; two ratios were thus established from one sample of selenite by comparison with silver and chlorine, and with metallic silver.

A study of all the known double bromides has been made, and new bromides of rubidium and cesium prepared. Of all the salts examined, the one which seems best adapted for the purpose of an atomic mass series is the ammonium salt. This substance is easily obtained pure and crystallizes well. When treated with hydroxylamine, selenium is set free, and the element itself can be brought on an asbestos filter, washed, dried at 100°, and weighed.

The use of hydroxylamine, according to the method of Dr. Harry F. Keller,[2] for the precipitation of selenium, affords the

[1] *Ann. chim. phys.*, (5), 10, 82.

[2] Private communication from the author.

clean and accurate determination that has long been desired by those who have used the tedious and uncertain precipitation by sulphurous acid or sodium sulphite in hydrochloric acid solution.

In many of the double halides which contain the ammonium group it has been possible to replace the ammonia by organic bases. This is especially the case in many of the salts of the metals of the platinum group. A series of salts has been prepared and studied in which the ammonia in ammonium bromoselenide has been substituted by fatty amines or aromatic bases. It was hoped that it would be possible to find a compound which would be of such character that it could be subjected to careful analysis. Such was not the case; none seemed to meet the demands imposed on them.

Finally a study was made of the monoxide of selenium, the existence of which has been repeatedly questioned.

FIRST SECTION.

HISTORICAL.

The atomic mass of selenium has been determined by a number of workers and by various methods. Figures have been obtained which range between 78.52 and 79.35 (O = 16).

The first to determine the atomic mass of this element was Berzelius.[1] He found that 100 parts of selenium, when treated with chlorine, gave 179 parts of the tetrachloride. If chlorine be 35.45, the atomic mass of selenium would be 79.22, from the single determination mentioned.

The next work was by Sacc,[2] who presents two series. The first includes three reductions of selenium dioxide with ammonium bisulphite and hydrochloric acid. This series gives selenium the atomic mass 78.68 (O = 16). The second series was obtained by treatment of barium selenite with sulphuric acid, and the subsequent weighing of barium sulphate. The mean of the four determinations gave 78.52 (O = 16, S = 32.07, Ba = 137.43).

[1] Pogg. *Ann.*, 8, 1.

[2] *Ann. chim. phys.* (3), 21, 119.

In 1852, Erdmann and Marchand[1] analyzed repeatedly sublimed and well-crystallized selenide of mercury, and obtained the figure 78.83 (Hg = 200); a value between that of Berzelius and Sacc.

Eight years later, Dumas[2] repeated the work of Berzelius, passing chlorine over selenium. He obtained the value 79.35 (Cl = 35.45).

In 1876, Ekman and Pettersson ignited silver selenite, metallic silver was obtained, which retained traces of selenium. Their result is 79.00 (Ag = 107.92). They also present a second series in which selenious acid was reduced by sulphur dioxide in the presence of hydrochloric acid. The selenium was brought on a glass filter and weighed. The second series gave a mean of 79.04 (O = 16).

DETERMINATION OF THE ATOMIC MASS OF SELENIUM BY THE HYDROCHLORIC ACID METHOD.

PREPARATION OF PURE SILVER BY THE METHOD OF STAS.

About 100 grams of ordinary pure silver were dissolved in hot dilute nitric acid. The solution was evaporated to dryness, the mass heated to the point of fusion, and held at that temperature until the oxides of nitrogen ceased to evolve. The cold residue was dissolved in water and this solution allowed to stand forty-eight hours, when it was run through a double filter to remove any suspended matter. After diluting the filtrate with thirty times its volume of distilled water, an excess of pure hydrochloric acid was added. The silver chloride was allowed to settle, after which it was washed by decantation with water containing a little hydrochloric acid, and finally with pure water. The silver chloride was collected on a cheese-cloth filter, pressed well and allowed to dry. When perfectly dry it was digested with aqua regia for several days, after which it was again washed by decantation with water. The pure silver chloride, thus prepared, was ready for reduction with milk-sugar and caustic potash. It was then necessary to purify the milk-sugar

[1] *J. prakt. Chem.*, 55, 202.
[2] *Ann. Chem. Pharm.*, 113, 32.

and potassium hydroxide, which were to be used in reducing the chloride to metal. The potassium hydroxide was heated to boiling and treated with a strong solution of potassium sulphide to precipitate any heavy metals which might be present. After filtration, the solution was treated with freshly precipitated silver oxide, and again filtered to remove the excess of potassium sulphide. The milk-sugar which was used was purified in a similar manner. The silver chloride was placed in a large porcelain casserole and covered with a solution of caustic potash and milk-sugar. The dish was exposed to a heat of 70°–80° until complete reduction had taken place. The silver appeared as a gray-white mass. It was washed with distilled water until the washings no longer gave an alkaline reaction, after which it was digested with dilute sulphuric acid, and finally washed with dilute ammonia. The silver thus obtained was mixed with five per cent. of its weight of fused borax and ten per cent. of sodium nitrate. This mixture was fused in a clay crucible. The metal obtained was snow-white in appearance. It was dissolved in nitric acid to a clear solution. This solution was evaporated to dryness and the resulting nitrate was obtained as a pure white mass.

PREPARATION OF PURE SELENIUM DIOXIDE.

Several hundred grams of quite pure selenium were treated with nitric acid. The resulting selenious acid was evaporated to hard dryness, when the dioxide was formed. This was dissolved in water, filtered through a double filter, hydrochloric acid was added and sulphur dioxide conducted into the warm solution. The selenium thus produced was washed with water, until the washings no longer gave an acid reaction, finally dried and fused. Broken lumps of this material were placed in a crystallizing dish on a water-bath heated to 70°. Pure nitric acid was added to cover the mass, a brisk evolution of nitrous fumes took place, and the selenium was oxidized to selenious acid. When all action appeared to be over, the solution was evaporated to dryness to remove the excess of nitric acid. The residue was dissolved in distilled water, and the solution transferred to a porcelain dish. The solution was then carefully evaporated on an iron plate, and the heat gradually increased

until the sublimation point of selenium dioxide (about the boiling-point of sulphuric acid) had been reached. When selenium dioxide began to sublime, a glass funnel, the neck of which had been closed with cotton, was placed over the dish, the base of the funnel resting on the inside of the dish and fitting closely. Selenium dioxide is thus sublimed and collects on the inside of the funnel as white needle-like crystals, often several inches long. The dioxide was resublimed three times. When an attempt is made to sublime selenium dioxide which is slightly impure, red selenium contaminates the otherwise white deposit. Traces of organic matter or other impurities, in slight amount, cause a red coloration, but when pure no reduction takes place during the sublimation. The long white needles were carefully removed from the funnel by means of a platinum spatula, and dissolved in distilled water. To this solution pure barium hydroxide was added until further addition failed to produce a permanent precipitate. Any sulphuric acid that might be present was thus removed along with any selenic acid. The solution containing the barium precipitate was allowed to stand over night, after which it was filtered. The clear solution was evaporated to dryness in a porcelain dish, the residue heated on an iron plate, and finally sublimed into a dry glass funnel as before. The clear needle-like crystals were picked out and resublimed three times. Selenium dioxide thus formed is perfectly stable in dry air, but in the ordinary atmosphere absorbs moisture rather rapidly.

PREPARATION OF SILVER SELENITE.

Selenium dioxide was dissolved in water, forming selenious acid. To this a solution of pure silver nitrate was added, slightly in excess. A few drops of selenious acid were added, when a complete precipitation of both silver and selenium takes place. The resulting white selenite of silver was thoroughly washed with water by decantation. The water was drained off as completely as possible, and the white mass dried by gentle heat. The powder was treated with pure nitric acid, one part to three parts of water, and heated. On cooling, silver selenite crystallizes from such an acid solution as an anhydrous salt, consisting of flat plates. These plates were broken up, washed

well with water, and again treated with dilute nitric acid. The salt was recrystallized three times. Finally the selenite was thoroughly washed with water and dried by heating to 70°–80° in an air-bath for twelve hours. The salt was carefully tested for nitrate and nitric acid, but none were found to be present.

A bottle of the material prepared was allowed to remain in direct light for a period of twelve months, and at the end of that time showed no discoloration.

By comparison of a known weight of the salt with pure benzene, the specific gravity of selenite of silver was found to be 5.9297.

DESCRIPTION OF APPARATUS.

Hydrochloric acid was prepared by the method which has been found very satisfactory in this laboratory, and consists in evolving the gas by adding concentrated sulphuric acid to concentrated aqueous hydrochloric acid. The hydrochloric acid was contained in a three-liter flask, and sulphuric acid was dropped on it from a separatory funnel. By regulating the current of sulphuric acid with a stop-cock, a constant evolution of gas is obtained at the ordinary temperature. Only pure acids were used, and such being the case, it was sufficient to dry the gas by passing it through two wash-bottles containing concentrated sulphuric acid, and a tower containing broken pieces of anhydrous calcium chloride. The dry gas was conducted through a combustion tube of hard glass, in which was placed a weighed quantity of silver selenite. The posterior portion of the tube was bent and directly connected by means of a stop-cock with a glass bulb containing water.

CORRECTIONS.

The weights used were carefully calibrated, first by comparison against each other, then against a normal weight. The larger weights were of brass, gold plated, the smaller ones being of platinum. All weights given have been reduced to vacuum. The following formula was used :

$$W = P + P\sigma\left(\frac{1}{\Delta} - \frac{1}{B}\right)$$

Where P = weight of substance,
σ = density of the air,
Δ = specific gravity of the substance,
B = specific gravity of the weights.

The balance used was a short-arm Becker, the sensibility of which was determined to be one-twenty-fifth of a milligram.

METHOD OF PROCEDURE.

By allowing gaseous hydrochloric acid to come in contact with selenium dioxide, A. Ditte[1] formed $SeO_2.2HCl$. He states that the compound consists of brilliant scales, which at 26° decompose into an amber-colored liquid of the composition $SeO_2.HCl$.

In performing the following experiments, the method of procedure was to weigh a definite amount of silver selenite into a previously weighed porcelain boat, introduce the boat into the combustion tube, and start the current of gas. After allowing the gas to pass over the salt for at least half an hour in the cold, a small flame was brought under the tube, and the boat gently heated. When the gas comes in contact with the selenite, rapid absorption takes place, the salt assuming a yellow color, due to the formation of the hydrochloride. In order to avoid any loss by spattering, as the salt becomes slightly moist, the boat was covered with a piece of platinum foil, and the heat increased very gradually. When it was thought that the selenium dioxide had been completely expelled, the tube was allowed to cool, and the boat removed to a desiccator containing soda-lime. After standing several hours, the silver chloride was weighed, replaced in the combustion tube and the gas conducted over it for one-half hour longer. The tube was again heated, and the chloride brought just to the point of fusion. It was again replaced in the desiccator, allowed to stand several hours, and reweighed. In all cases the weights of the boat before and after this second treatment were the same, a point which seems to indicate that silver chloride sustains no perceptible loss when brought to the point of fusion. The silver chloride was tested for selenium, but none was found.

[1] *Ann. chim. phys.*, (5), 10, 82.

Ag_2SeO_3. Grams.	AgCl. Grams.	Se. Atomic mass.
0.98992	0.82715	79.326
1.59912	1.33600	79.373
2.70573	2.26087	79.320

Mean = 79.339
Probable error = ±0.011

Having thus demonstrated that hydrochloric acid gas will completely drive out selenium dioxide from silver selenite, leaving behind pure chloride, according to the equation,

$$Ag_2SeO_3 + 4HCl = 2AgCl + SeO_2.2HCl + H_2O,$$

the next step was to reduce the chloride formed by this reaction to metal.

SECOND SERIES.

Hydrogen gas was generated by the action of dilute sulphuric acid on mossy zinc. The gas was purified by conducting it through a series of wash-bottles; the first containing silver sulphate; the second, potassium permanganate; the third, lead nitrate; and the fourth, caustic potash. It was then dried by passing through sulphuric acid. The pure gas was conducted through a tube of porcelain in which the reduction took place. The excess of hydrogen and the hydrochloric acid formed were passed through a wash-bottle containing sulphuric acid, following which was a wash-bottle containing water to absorb the hydrochloric acid. The unused hydrogen was allowed to escape into the room.

The boat containing the silver chloride, after being weighed for comparison with silver and oxygen, was introduced into the porcelain tube, all connections were closed and a brisk current of hydrogen conducted through the apparatus. When the hydrogen was free from air, the combustion furnace, containing the porcelain tube, was started and the heat gradually increased until the outside of the tube attained bright redness. This temperature was maintained for a period of three hours, when the tube was allowed to partially cool, the boat and its contents were removed to a desiccator. After standing several hours, it was weighed, replaced in the combustion tube, and hydrogen again conducted over it at a red heat for an hour. The boat was again removed to a desiccator, cooled as before, and reweighed.

The weights before and after reignition in hydrogen were in all cases the same. After the last weighing, the boat and contents were treated with pure dilute nitric acid and warmed. Complete solution ensued, showing the reduction of silver chloride to metallic silver had been complete. Tests were made for selenium in the resulting solution, but none was found.

Ag_2SeO_3. Grams.	AgCl. Grams.	Se. Atomic mass.	Ag. Grams.	Se. Atomic mass.
0.26204	0.21897	79.299	0.16480	79.356
0.58078	0.48522	79.371	0.36534	79.280
0.70614	0.58999	79.350	0.44417	79.301
0.80811	0.67532	79.282	0.50821	79.369
0.98396	0.82232	79.263	0.61882	79.358
1.29685	1.08350	79.361	0.81562	79.277
1.63103	1.36288	79.316	1.02588	79.320
2.00162	1.67234	79.358	1.25884	79.357
		Mean 79.325		Mean 79.329
		Probable error ±0.009		Probable error ±0.009

EXPERIMENTS WITH SODIUM SELENITE.

In order to ascertain if the alkaline selenites would prove as well adapted for treatment with hydrochloric acid gas as the silver salt, a study was made of sodium selenite.

Sodium carbonate was purified by recrystallization several times. It was found, when tested, to be free from sulphate, chloride, and silicate. The salt was fused in a platinum crucible under a blast-lamp. Equivalent weights of the carbonate and selenium dioxide were dissolved in water, the solutions combined and evaporated to dryness. The salt obtained was recrystallized seven times from water. Crystallization takes place only when the liquid has attained the consistency of a thick sirup. The salt obtained in this manner, when treated with dilute hydrochloric acid, showed the presence of a slight amount of carbonate, hence was rejected.

An attempt was made to prepare the sodium salt by ignition of the acid selenite. In this case, a salt of constant composition could not be obtained. At a temperature slightly above that of complete conversion into neutral selenite, the salt appears to lose slight amounts of selenium dioxide, varying with the temperature.

DETERMINATION OF THE ATOMIC MASS OF SELENIUM BY ANALYSIS OF AMMONIUM BROMOSELENATE.

In the following part, devoted to the double bromides, a study has been made of a large number of derivatives. It is sufficient to state here that the salt found most suitable for careful analysis is the double bromide of ammonium and selenium. A description of the properties of the salt is entered into more fully in Section II.

PREPARATION OF PURE BROMINE.

Bromine was purified by distillation over manganese dioxide and concentrated sulphuric acid. A retort containing this mixture was heated on a water-bath and the distillate collected in a chilled receiver. This product was brought in contact with manganese dioxide and again distilled. Having started with pure bromine of commerce, chlorine and organic matter would, if present, be eliminated by this procedure.

AMMONIUM BROMIDE.

So-called "pure" ammonium bromide was twice recrystallized, the crystals dried each time by pressing between pieces of filter-paper. It was then twice sublimed and again crystallized. The salt was allowed to remain for several days in a desiccator to become thoroughly dry. Thus obtained, ammonium bromide is pure white, dissolves in water to a clear colorless solution, and on ignition leaves no residue.

SELENIUM.

Selenium dioxide, purified in the manner previously described, was dissolved in water containing hydrochloric acid. Sulphur dioxide, generated by the action of sulphuric acid on copper turnings, was washed by sulphuric acid and conducted into the warm solution. Selenium was precipitated. It was washed with hot water until the washings no longer gave an acid reaction. After drying it was fused to the black glassy modification. While yet liquid, the mass was poured from the crucible in which it had been fused, on a porcelain plate, allowed to cool, and finally broken into small fragments.

AMMONIUM BROMOSELENATE.

Nine and eight-tenths parts of ammonium bromide were dissolved in water; to this solution four parts of selenium were added, bromine was introduced till in slight excess, and perfect solution had ensued. The solution of ammonium salt was brought on a water-bath, the excess of bromine expelled and allowed to slowly evaporate, when ammonium bromoselenate separated. The crystals were removed from the mother-liquor, dried by pressing between filter-paper, dissolved in water containing hydrobromic acid, which had been repeatedly distilled, and allowed to crystallize at the temperature of a water-bath. The crystallization was repeated several times. Finally, the salt was placed in a desiccator containing soda-lime where it remained several days. Examined under the microscope, the red crystals showed no admixture of ammonium bromide. The specific gravity of the salt was determined in benzene and found to be 3.3266.

METHOD OF PROCEDURE.

A weighed quantity of the salt is dissolved in water, and to this is added a few cc. of ammonia. Pure hydroxylamine hydrochloride is introduced in slight excess, when a reaction takes place, probably as expressed in the following equation:

$$SeO_2 + 6NH_2OH = Se + 2NH_3 + 6H_2O + 2N_2O.$$

Selenium appears in the cold as a flocculent red precipitate. The solution is gradually warmed to expel free ammonia, and render the solution neutral. Under the influence of heat the precipitated selenium changes to the gray variety. The precipitate is brought upon asbestos felt, prepared by pouring asbestos suspended in water into a Gooch crucible, and sucking hard and dry by means of a good filter-pump. This filter, having been ignited and weighed, the solution containing the selenium is poured upon it, the selenium washed thoroughly with hot water, dried for two hours in an air-bath heated to 100°, and allowed to cool in a desiccator. The increase in weight of the crucible represents the selenium in the original salt. All of the filtrates were preserved, evaporated together, and tested for selenium, but none could be detected, showing the precipitation was complete.

$(NH_4)_2SeBr_6$. Grams.	Se. Gram.	Se. Atomic mass.
1.00059	0.13324	79.243
1.50153	0.20022	79.367
2.00059	0.26649	79.273
2.00126	0.26657	79.269
3.00125	0.39958	70.226
4.00216	0.53346	79.333
5.00218	0.66656	79.306
5.03001	0.66998	79.267

Mean 79.285
Probable error = ±0.011

Mean from silver chloride, 79.329 (11 determinations).
Mean from metallic silver, 79.329 (8 ").
Mean from analysis of ammonium bromoselenate, 79.285 (8 ").
Giving a general mean, 79.314

The values used in calculation are those given by Clarke (Atomic Weights, 1897), and are as follows :

Ag	107.92
Br	79.95
Cl	35.45
O	16.00
N	14.04
H	1.008

The mean of all determinations is close to the values obtained in the synthesis of selenium chloride being slightly higher than the determination by Berzelius and a trifle lower than the series of Dumas.

From selenite of silver values are presented from quantities, the greatest of which is ten times the least, the difference in the ratio obtained in these extremes being but slight. In the series obtained from ammonium selenium bromoselenate, the maximum quantity used is five times that of the minimum.

That the mean of the series from silver selenite approaches very closely the true atomic mass of selenium, can be little doubted. The values obtained in the reduction of silver chloride to metal express the commonly accepted ratio between silver and chlorine.

Selenium was shown to be completely removed from silver selenite by hydrochloric acid, and complete reduction of silver chloride to metal was proved in every instance. These facts

seem to afford good proof of the reliability of the hydrochloric acid method and the subsequent reduction process.

The advantages this method possesses over those used by previous workers is, first, the great reduction of the factor of personal error, in that the only part in which the operator is directly concerned is the weighing of material and product; second, the establishment, from one weight of starting material, of two values, whose mutual agreement depends on their similarity to a well-established ratio. The latter point indicates that the ratios prove themselves.

Additional evidence that the atomic mass of selenium is very close to the value given by the silver salt is furnished by the analysis of ammonium bromoselenate. This latter salt is easily obtained pure, and by decomposition with a reducing agent such as hydroxylamine, selenium itself can be weighed. In contrast to the previous method, the manipulation of the operator must needs play a great part, yet the satisfactory precipitation of selenium by hydroxylamine seems to be a strong point in its favor.

SECOND SECTION.

INVESTIGATION OF THE DOUBLE BROMIDES.

Considerable attention has been drawn to the double bromides of tellurium by Wheeler.[1] Earlier work was done in the same line by Berzelius,[2] Rammelsberg,[3] and von Hauer.[4] Little was done on the corresponding derivatives of selenium, until Muthmann and Schäfer[5] prepared the double bromides of selenium with potassium and ammonium. The chlorides have received but little attention, and from what little has been done, they are known to be difficult to prepare. The double bromides are well-defined crystalline salts. The combination which takes place between selenium tetrabromide and certain of the alkaline bromides is so definite as to lead to the view that they are salts

[1] *Am. J. Sci.*, [3], **45**, 267.
[2] Pogg. *Ann.*, **32**, 577.
[3] *Ber. Monats. Ber.*, *1875*, 379.
[4] *J. prakt. Chem.*, **73**, 98.
[5] *Ber. d. chem. Ges.*, **26**, 1008.

of hydrobromoselenic acid. Like the tellurium salts, they follow but one type, Me_2SeBr_6.

By examining these double salts, it was thought one or more might be found, which would answer the requirements of a starting material for the determination of the atomic mass of selenium. To this end a study has been made of the inorganic salts, and a number containing organic groups have also been prepared. Of all the salts examined, the most satisfactory one was the ammonium salt. The pyridine derivative appears as beautiful red scales, but the fact that it is only possible to obtain the salt from alcoholic solution, and that it is likely to suffer secondary decompositions, seemed to be an objection to its use in accurate analysis.

The method Muthmann and Schäfer employed in the preparation of the bromoselenates of potassium and ammonium was to treat selenium dioxide with hydrobromic acid, when a solution of selenium tetrabromide was formed. To this they added a saturated solution of potassium or ammonium bromide, and boiled. On cooling, a dark orange red powder separated, which contained octahedral crystals of bromoselenate.

A simpler and more convenient method of procedure was found to consist in adding bromine directly to a solution of the alkaline bromide, in which had been introduced the amount of selenium requisite to form the desired bromoselenate. The reactions took place in the following manner: Bromine coming in contact with selenium formed a dark layer of liquid monobromide, which being heavier than the solution, remained at the bottom of the vessel. Further addition of bromine converted the monobromide into tetrabromide, which reacting with the alkaline bromide present, formed bromoselenate. These reactions were all accompanied by evolution of heat. The excess of bromine was expelled on a water-bath, and on evaporation beautiful red crystals of bromoselenate separated. This method was found to be readily applicable in the preparation of inorganic bromoselenates.

In many double salts in which the ammonium group plays the part of alkaline metal, it is possible to replace the ammonia by an amine or aromatic base. In the case of platinum salts this takes place with ease, and subsequent experiments will

show that tetrabromide of selenium unites with the salts of the fatty amines and aromatic bases to form well-defined analogous salts.

In the preparation of the organic derivatives recourse must be had to another means of preparation, since bromine in free condition acts on the organic bodies themselves.

INORGANIC SALTS.

Potassium Bromoselenate.—This salt was prepared by the method above indicated, and was found to possess the same composition and properties as observed by Muthmann and Shäfer.

Sodium and Lithium Salts.—When the bromides of lithium and selenium or sodium and selenium are brought together, the mutual affinity is so small that no union occurs. On evaporating a solution of a mixture containing the respective salts, only alkaline bromide and selenious acid separated; neither exercise a sufficiently strong influence on the selenium to enable it to hold its bromine.

Rubidium Bromoselenate.—Pure rubidium bromide, tested spectroscopically and found to be free from cesium and potassium, was dissolved in water, selenium added, and bromine introduced. On evaporation at the low temperature of a water-bath, red crystals appeared, which examined under the microscope[1] showed the isometric combinations of cube and octahedron. In polarized light they proved to be isotropic.

On being subjected to analysis, the following data were obtained:

Salt. Gram.	Se. Gram.	Se. Per cent.
0.5015	0.0539	10.74
0.4999	0.0540	10.80
Salt. Gram.	**AgBr. Gram.**	**Br. Per cent**
0.5012	0.7760	65.88

The formula Rb_2SeBr_6 requires 10.82 per cent. Se and 65.72 per cent. Br.

The values used in calculation were: Rb = 85.43, Se = 79.3, Br = 79.95.

[1] The microscopic examinations were made with the assistance of Professor A. P. Brown, and to him the author is indebted.

Cesium Bromoselenate.—Cesium carbonate was dissolved in pure hydrobromic acid, and the resulting bromide crystallized. When examined with the spectroscope this salt showed absence of potassium and rubidium salts. On treatment of the salt with selenium tetrabromide, there appeared on evaporation crystals similar, in appearance and properties, to the salts of rubidium and potassium.

Analysis gave:

Salt. Gram.	Se. Gram.	Se. Per cent.
0.5009	0.0479	9.56

Salt. Gram.	AgBr. Gram.	Br. Per cent.
0.5007	0.6860	58.29

Calculated for Cs_2SeBr_6, 9.73 per cent. Se, 58.16 per cent. Br. Cs = 132.89, Se = 79.3, Br = 79.95.

These salts are all soluble in water to a colorless solution. With the rise of atomic mass of the basic element, the solubility decreases, the rubidium salt being less soluble in water than the potassium salt, while the cesium salt is rather insoluble. This property may be expected, since the alums, and particularly the chloroplatinates of these positive elements show a corresponding decrease in solubility as the atomic mass rises.

Attempts were made to prepare the bromoselenates of barium and cadmium, but like sodium and lithium, these salts do not appear to exist.

The salts of thallium, in the lower state of oxidation, in many cases closely resemble the alkali salts, such as in the formation of double platinum salts, etc. No bromoselenate seems to exist. Selenium tetrabromide, prepared from this dioxide and hydrobromic acid, and hence obtaining no free bromine, tends rather to oxidize thallous salts to the thallic state than to form double salts.

Ammonium bromoselenate was prepared in a manner similar to that of the salts of rubidium and cesium. It is less soluble in water than the potassium salt. Analysis indicated the composition $(NH_4)_2SeBr_6$. The crystals exhibit the same isometric combination of cube and octahedron that the salts of potassium, rubidium, and cesium show. The salt was considered to be

well adapted to accurate analysis, since ammoninm bromide can be readily obtained pure both by sublimation and crystallization.

Analysis of the preceding salts was made by determining the bromine by precipitation with silver nitrate, in presence of sufficient free nitric acid to hold in solution the silver selenite which is simultaneously formed. The selenium was precipitated by hydroxylamine, and after washing with hot water, was brought upon an asbestos filter, dried at 100° and weighed.

ORGANIC SALTS.

For the preparation of the organic derivatives two methods were found to be available. The first consisted in preparing selenium tetrabromide by direct bromination of finely divided selenium, with the vapors of bromine. Red crystals of tetrabromide were formed, which are very soluble in alcohol to a red brown color. When a concentrated alcoholic solution of the amine salt is treated with a strong alcoholic solution of tetrabromide, a precipitate is produced which consists of bromoselenate of the amine. This precipitate was dissolved in alcohol containing hydrobromic acid, and the resulting colorless solution allowed to crystallize spontaneously. Crystallization can be greatly hastened by placing the solution in a desiccator containing soda-lime, and exhausting the air.

A second method employed and a more satisfactory one, was to treat selenium dioxide with concentrated hydrobromic acid. Alcohol was added to the solution to take up the excess of water. By treating the amine salt dissolved in alcohol with this tetrabromide, salts were obtained identical with those obtained by the former method. The latter method is by far the cleaner method and the one to be preferred.

As a rule, the organic salts in appearance closely resemble the alkaline salts; they generally consist of fine red powder. Water decomposes them, hence they cannot be crystallized from it. Prolonged action of ether, more rapidly when warm, extracts selenium bromide.

Methylamine Bromoselenate. — Methylamine hydrochloride, containing ammonium salts, was treated[1] with caustic soda and distilled; the vapors were collected in dilute sulphuric acid. The

[1] Fleck: This Journal, 18, 670.

neutral solution of mixed sulphates of ammonium and methylamine was evaporated to dryness, and the residue extracted with absolute alcohol. Ammonium sulphate remained insoluble, methylamine sulphate passing into solution. After filtration, the alcohol was evaporated, the sulphate treated with sodium hydrate, when methylamine was liberated in pure condition. The gas was collected in hydrobromic acid. This latter solution, on evaporation, yielded pure methylamine hydrobromide.

When methylamine bromide was treated in alcoholic solution with selenium tetrabromide, a red precipitate formed, which on recrystallization from alcohol containing hydrobromic acid, gave a very finely crystalline body, which analyzed as follows:

Salt. Grams.	Se. Gram.	Se. Per cent.
1.0067	0.1266	12.57
Salt. Gram.	**AgBr. Grams.**	**Br. Per cent.**
0.9874	1.7829	76.83

The formula $(CH_3NH_3)_2SeBr_6$ requires Se 12.72 per cent. and Br 76.96 per cent. The values used in calculation were: H = 1.008, C = 12.01, N = 14.04, Se = 79.3, Br = 79.95.

Ethylamine Bromoselenate.—This salt was prepared from ethylamine bromide and selenium tetrabromide in a manner similar to the salt of methylamine. It forms flat hexagonal prisms, red in color. Analysis gave:

Salt. Grams.	Se. Gram.	Se. Per cent.
1.0008	0.1215	12.14
Salt. Gram.	**AgBr. Gram.**	**Br. Per cent.**
0.5619	0.9713	73.55

The formula $(C_2H_5NH_3)_2SeBr_6$ requires Se 12.17 per cent. and Br 73.66 per cent.

Dimethylamine Bromoselenate.—Dimethylamine was prepared by boiling nitroso-dimethylaniline with caustic soda; quinone oxime was formed, while at the same time dimethylamine was evolved as a gas, and collected in dilute acid. A good yield was obtained by this method. The salt obtained was again distilled with sodium hydroxide and the gas absorbed in dilute

hydrobromic acid. After crystallization the bromide was dissolved in alcohol and treated with selenium tetrabromide. On allowing the alcoholic solution to evaporate, red crystals were obtained, similar in appearance to the salt of methylamine.

Analysis gave :

Salt. Grams.	Se. Gram.	Se. Per cent.
1.0233	0.1251	12.22

Salt. Gram.	AgBr. Gram.	Br. Per cent.
0.5227	0.9049	73.66

$[(CH_3)_2NH_2]_2SeBr_6$ is an isomeride of ethylamine bromoselenate and like it requires Se 12.16 per cent. and Br 73.66 per cent.

Trimethylamine Bromoselenate. — Trimethylamine was freed from contaminating ammonium salts, by treatment of the mixed sulphates with absolute alcohol, when the amine salt dissolves, leaving ammonium sulphate insoluble. Trimethylamine was liberated by treatment of the sulphate with caustic soda and absorbing the free amine in hydrobromic acid. The bromoselenate was prepared by adding a solution of selenium tetrabromide to trimethylamine bromide, dissolved in alcohol. The red precipitate formed was recrystallized from alcohol, when a fine red crystalline powder was obtained.

Analysis gave:

Salt. Grams.	Se. Gram.	Se. Per cent.
1.0010	0.1195	11.93

Salt. Grams.	AgBr. Grams.	Br. Per cent.
1.0501	1.7406	70.53

A determination of nitrogen by the Kjeldahl method gave 4.18 per cent. N. The formula $[(CH_3)_2NH]_2SeBr_6$ requires Se 11.68 per cent., Br 70.62 per cent., and N 4.13 per cent.

Tetraethyl Ammonium Bromoselenate.—The bromide was prepared by treating the base with hydrobromic acid. The bromoselenate was prepared in the same manner as previously described salts and crystallizes from alcoholic solution in minute flat hexagonal plates.

Analysis gave:

Salt. Grams.	Se. Gram.	Se. Per cent.
1.0021	0.0991	9.89

Salt. Gram.	AgBr. Gram.	Br. Per cent.
0.5366	0.7391	58.60

The formula $[(C_5H_5)_4N]_2SeBr_6$ requires Se 9.67 per cent. and Br 58.53 per cent.

It thus appears that all of the hydrogen atoms in ammonium bromoselenate can be replaced by a fatty amine. An entirely different behavior is shown by the aromatic amines. Aniline hydrobromide in hydrobromic acid solution precipitates selenium completely from a solution of selenium tetrabromide.

When an alcoholic or aqueous solution of selenium tetrabromide is treated with hydrobromide of aniline and filtered, the filtrate is found to be free from selenium, showing complete precipitation has taken place.

As might be expected from this behavior of aniline, diphenylamine in hydrobromic acid solution forms no derivative with selenium tetrabromide.

In the many reactions that were tried with phenylhydrazine, it appears that this substance seems to be almost as good a reagent for the precipitation of selenium as hydroxylamine.

Pyridine Bromoselenate.—Both pyridine and quinoline are strongly basic bodies of the aromatic series; the first forms a well-defined bromoselenate, while the second forms a compound which decomposes so readily with the separation of selenium that it is impossible to analyze it.

On treating pyridine hydrobromide in alcoholic solution with selenium tetrabromide, a crystalline precipitate is produced, which, recrystallized from alcohol, forms beautiful deep red scales. Under certain conditions it is possible to obtain the salt as prismatic crystals. This salt, like the salts of the fatty amines, dissolves in water to a colorless solution. Water, benzene, chloroform, ether, and carbon bisulphide dissolve in salt, but on evaporation of the solvent decomposition takes place, selenium separating. It has only been possible to obtain the salt from alcoholic solution.

A complete analysis was made; carbon and hydrogen were

determined by combustion. Nitrogen was determined by the method of Dumas.

Salt. Grams.	Se. Gram.	Se. Per cent.
1.0011	0.1121	11.19

Salt. Grams.	AgBr. Grams.	Br. Per cent.
0.5007	0.7846	66.63
1.0057	1.5769	66.71

Salt. Gram.	H_2O. Gram.	H. Per cent.
0.4006	0.0645	1.79

Salt. Gram.	CO_2. Gram.	C. Per cent.
0.4006	0.2465	16.75

0.5151 gram of the salt gave 17 cc. of nitrogen, equivalent to 4.14 per cent.

The formula $(C_5H_5NH)_2SeBr_6$ requires H 1.67 per cent., N 3.90 per cent., Se 11.02 per cent., C 16.74 per cent., and Br 66.69 per cent.

Unless a slight excess of selenium tetrabromide is present in the solution undergoing crystallization, the salt dissociates to a slight degree. This fact and the tendency it showed to lose bromine, when dried over soda-lime, seem to be serious objections to its employment in an atomic mass determination.

Piperidine Bromoselenate.—Like pyridine, piperidine yields a strongly crystalline body with selenium tetrabromide. The salt was prepared in a manner similar to that of the pyridine salt. When crystallized from alcohol red tabular crystals appeared.

Analysis gave:

Salt. Gram.	Se. Gram.	Se. Per cent.
0.5002	0.0540	10.79

Salt. Gram.	AgBr. Gram.	Br. Per cent.
0.5305	0.8161	65.46

Salt. Gram.	CO_2. Gram.	C. Per cent.
0.4004	0.2422	16.49

Salt. Gram.	H_2O. Gram.	H. Per cent.
0.4004	0.1369	3.52

The formula $(C_5H_{11}NH)_2SeBr_6$ requires H 3.30 per cent., N

3.84 per cent., Se 10.84 per cent., C 16.46 per cent., and Br 65.59 per cent.

On standing over soda-lime, this salt, like the pyridine compound, slowly loses bromine.

When the mother-liquor from which the red soluble crystals were obtained was allowed to slowly evaporate, a black salt appeared, from which, when treated with water, large quantities of selenium immediately separated. Analysis of various samples of this black compound gave determinations of selenium from 11.79–14.39 per cent. Bromine estimations indicated a variation in content from 67.42 per cent. to 70.71 per cent. From the irregularities in composition of different samples and the variations in color from red to black, it would appear that piperidine bromoselenate, when crystallized from solutions containing an excess of selenium tetrabromide, tends to enclose the latter and carry it down with it.

THIRD SECTION.

SELENIUM MONOXIDE.

Different chemists at various times have either affirmed or denied the existence of the monoxide of selenium. Berzelius ascribes the odor of rotten horseradish, noticed when selenium burns in air, to the existence of this oxide. Chabrie,[1] in his work on the organic derivatives of selenium, claims to have prepared the monoxide by heating selenium to 180° in air. So firmly convinced was he that the monoxide exists that he used this method as a means of estimating selenium. A. W. Pierce[2] has made an investigation of Chabrie's work, and concludes that it is probably not formed by the method of Chabrie, and thinks the odor produced when selenium is burned in air is due to the presence of moisture, which, under the circumstances, would produce hydrogen selenide.

While subliming the large quantities of pure dioxide used in the preceding investigation, at no time was there noticed an odor like that produced when selenium burns in air or when a selenide is roasted. On the contrary, the vapor of selenium

[1] *Ann. chim. phys.* [6], 20, 273.
[2] *Ztschr. anorg. Chem.*, 13, 121.

dioxide which at times escaped into the air, gave an odor much resembling that of sulphur trioxide.

An experiment was made to determine whether selenium would reduce the dioxide when heated in an open vessel at the atmospheric pressure. No combination was found to take place.

A second experiment was made, in which equivalent parts by weight of selenium and dioxide were placed in a stout glass tube of hard glass, about forty inches long by one-half inch internal diameter. The tube was sealed and heated in a large flame, until the selenium melted. The dioxide under the pressure generated by its own volatilization, melted to a thick liquid. The temperature was raised to the boiling-point of selenium. Should selenium be able to reduce the dioxide, it should do so in a solution of the combined gases. Such, however, is not the case; on cooling, the mass resolves itself into separate layers of selenium and dioxide. When the tube was opened, no pressure was observed (such as would have been the case had a gas been formed), nor could any odor be detected. On treating the mass with water, selenious acid was formed, which dissolved, leaving selenium insoluble.

Selenium and tellurium have many derivatives from which well-established analogies can be drawn. Where a derivative of one element exists, a corresponding derivative of the other is usually found. That tellurium forms a monoxide, there can be little doubt, hence it has seemed probable that a monoxide of selenium should exist. However, in considering their halides, we find that while tellurium forms the compounds TeX_2 and TeX_4, directly analogous to the oxides TeO and TeO_2, selenium forms only those halides of the types Se_2X_2 and SeX_4, the latter corresponding to the well-known SeO_2. From the analogy thus established between the oxygen and halogen derivatives, one would rather expect an oxide Se_2O than SeO. It was therefore thought that the lower oxide might be prepared by treatment of the monobromide with dry silver oxide. Se_2Br_2 was prepared by rubbing the tetrabromide with selenium. No action could be brought to take place between silver oxide and a solution of the bromide in carbon disulphide. When the liquid bromide is treated at the ordinary temperature with silver oxide, a violent reaction takes place. Much heat is evolved, the reaction being

explosive in character. The resulting mass on treatment with water gives a solution containing only selenious acid.

If the monoxide is formed it is likely that the heat of the reaction would decompose it. The experiment was subsequently modified by chilling the bromide to $-7°$. At this temperature, silver oxide swims unattacked on the surface of the liquid monobromide. No reaction takes place until the whole attains a temperature of $+20°$, when the same violent reaction takes place that was before noted. On conducting the experiment in a closed tube, it is noticed that on opening the tube, no pressure exists, hence it is unlikely that a gas has been formed. Should a lower oxide be formed at all in this reaction, the experiments seem to indicate that it immediately dissociates into selenium and the dioxide.

As Pierce has pointed out, it seems very likely that the odor noticed when selenium is roasted in air, is due to the presence of hydrogen selenide, and that efforts to obtain other oxides than the dioxide, thus far have been unsuccessful.

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OSMOTIC PRESSURE.

BY C. L. SPEYERS.

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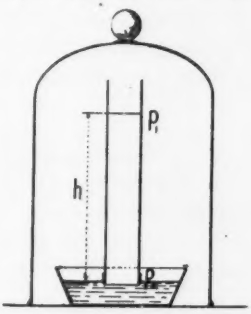
CONSIDER the following arrangement: The lower vessel contains pure solvent; the tube contains a solution of some non-volatile body in that solvent. The tube is open at the



top but closed at the bottom by a diaphragm permeable to the solvent only. At equilibrium, the arrangement is to be so

adjusted that the diaphragm is just at the surface of the solvent in the outer vessel. The tube and vessel holding the solvent are covered by a bell jar, the air being removed so that the only aeriform body under the bell jar is the vapor of the solvent. This is the arrangement described by Arrhenius.[1] At equilibrium, the counter pressure preventing the entrance of the solvent, is commonly given as equal to hs on the unit surface, h being the height of the column of liquid and s the density of the solution whose counter pressure balances the osmotic pressure, π, so that at equilibrium

$$\pi = hs \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

The difference between the pressure of the vapor on the top of the solution and the pressure of the vapor on the pure solvent in the lower vessel is so slight compared with π that for our purpose it is negligible. Likewise the coefficient of compressibility of solvent may be neglected by us.

The value of h is *a priori* unknown, but when the system reaches equilibrium, then h must have such a value that the vapor-pressure of the solution equals the vapor-pressure of the pure solvent at height h.

Now

$$dp = -s'dh$$

where s' is the density of the vapor compared with hydrogen.

Experiments by Ramsay and Young, quoted by Noyes and Abbot,[2] show that the density of ether vapor at 12.9° and under pressure p in terms of hydrogen at the same temperature and under the same pressure is $36.08 + 0.0581\,p$. One cc. hydrogen at 12.9° and under p pressure weighs $(0.0_4 8987p/76)\ 273/283.9$ grams.

$$s' = 0.0_4 8987 \frac{p}{76} \cdot \frac{273}{283.9} (36.08 + 0.0581p) \text{ grams.}$$

Wherefore, for ether as solvent,

$$h = \frac{76 \cdot 285.9}{0.0_4 8987 . 273} \int_{p_1}^{p_0} \frac{dp}{p(36.08 + 0.0581p)} \text{ cm.}$$

[1] *Ztschr. phys. Chem.*, **3**, 115 (*1889*).
[2] *Ibid.*, **23**, 56 (*1897*).

Integrating by partial fractions, we get

$$h = 24540\, l_e \frac{p_0(36.08 + 0.0581p_1)}{p_1(36.08 + 0.0581p_0)} \text{ cm.}$$

Substituting in 1 we get

$$\pi = 24540 \cdot 13.60\, sl_e \frac{p_0(36.08 + 0.0581p_1)}{p_1(36.08 + 0.0581p_0)} \text{ in grams} \ldots . (2)$$

The next step is to substitute for s, which in this case is to refer to ether.

Now this little paper centers around this quantity s. I wish to show that for s we should substitute the value for the pure solvent, in this case ether, and not the value for the solution which is in the tube at the time of consideration. This latter value was used by Arrhenius.[1]

Does not the great advantage of the modern theory of solution lie in the notion that the constituents of a liquid homogeneous mixture, are independent of each other? Is not this far more suggestive than the assumption of a peculiar, characteristic, almost chemical, action between the constituents, which assumption even the originators of the modern theory of solution seem at times inclined to make? For when the constituents are independent of each other, then we must seek the apparently peculiar characteristic action of one constituent upon the other constituent of a homogeneous liquid mixture, in a difference of condition offered by the one constituent to the other. For instance, suppose we have ammonium chlorid in the form of partially dissociated vapor and we introduce some nitrogen, keeping temperature and total pressure constant. Then the ammonium chloride is believed to dissociate still more; but not because the nitrogen acts chemically upon this system or in any other characteristic way upon it. Not at all. But because the introduction of nitrogen necessitates a change in the condition of the system. Of course the change in condition in this case is readily detected, whereas the changes in condition produced when one of the constituents of a homogeneous liquid mixture is changed are not so easily followed up. Nevertheless, it would seem more profitable to seek for the cause of apparently specific

[1] *Loc. cit*

action in this direction rather than in the direction of chemical affinity or chemical action; the latter notion is so vague.

Granting this independence of the constituents, the notion of a diaphragm permeable to one constituent but not to the other, becomes clear enough.

In the arrangement considered above, the diaphragm is permeable to the constituent present in larger quantities and therefore generally called the solvent. In this case ether is the solvent. As the diaphragm is impermeable to the solute, should we not claim that it receives the full pressure of the solute, not allowing any activity on the part of the solute to pass through the diaphragm? How can we claim anything else? But then when we do this, how can we claim that the hydrostatic pressure preventing the entrance of the ether, comes from anything else than the column of pure ether in the solution, which column of pure ether has the height of the column of solution? We cannot, consistently, with what we have assumed regarding the independence of the constituents of the liquid mixture. For we are not to look upon a molecule of ether locked to a molecule of solute, so that whither the ether molecule goes, the other molecule must go. Not at all, not even for an instant. And yet, how can we mean otherwise when we say that s in equation (1) shall refer to the solution as a whole and not to the solvent in it.

Now in the paper of Noyes and Abbot[1] from which paper the above calculations have been taken, there is a collection of data which will be useful in testing this view.

In that paper they describe an arrangement which we must look upon as purely imaginary; the arrangement cannot be looked upon as possible in fact, though perhaps interesting from a theoretical point of view. Instead of putting the diaphragm at the bottom of the tube, they put it at the top of it and assume that the pure solvent rises in the tube until its hydrostatic pressure balances the osmotic pressure of the solute. But in their development of the necessary formulas, they do not take into account the external air pressure needed to force up the column of liquid supposing the arrangement to be subject to the air-pressure, or if in a partial vacuum such as we have assumed in our arrangement, they do not show how such a column of

[1] *Loc. cit.*

liquid could possibly rise in the tube, for the difference in pressure, $p_0 - p_1$, is insignificant compared with π. In either case, so far as their results depend upon their theoretical deductions, they are valueless, but considered by themselves, the data are very valuable, and will serve us a good turn.

Substituting in (2) the value for s for pure ether, given by Noyes and Abbott, equal to 0.7206, and passing to Briggs' logarithms, we get

$$\pi = 553900\left(l\frac{63.08 - 0.0581p_1}{p_1} - 0.0607\right) \cdots\cdots (3)$$

On the other hand, knowing the concentration, we can calculate π by Avogadro's law. The two values should agree. In the following table, largely from Noyes and Abbot, c is the quantity of solute, in one series naphthalene, in the other azobenzene, in one part of ether at 12.9°, p is the vapor-pressure of the solution in cm. of mercury, s is its density, π_1 is the osmotic pressure calculated from (3), π_2 is the osmotic pressure calculated from (3) but substituting the density of the solution for the density of the pure solvent, π_0 is the osmotic pressure calculated according to Avogadro's law, $\Delta\pi_1$ is the percentage variation of π_1, compared with π_0 as the standard, $\Delta\pi_2$ is the percentage variation of π_2, compared with π_0 as the standard.

c_0	ϕ naphthalene.	ϕ azobenzene.	s naphthalene.	s azobenzene.	π_1 naphthalene.	π_1 azobenzene.	π_2 naphthalene.	π_2 azobenzene.	π_0 naphthalene.	π_0 azobenzene.	$\Delta\pi_1$ naphthalene.	$\Delta\pi_2$ naphthalene.	$\Delta\pi_1$ azobenzene.	$\Delta\pi_2$ azobenzene.
0.00	33.05	33.05	0.7206	0.7206	....	.....	.....	.....	....	.....	.....	.....	....	....
0.01	32.82	32.91	0.7232	0.7234	1495	886.2	1500	889.4	1347	947.6	+11.0	+11.0	—6.9	—6.1
0.02	32.62	32.77	0.7258	0.7262	2880	1938.0	2901	1953.0	2673	1883.0	+7.7	+8.5	+2.8	+3.7
0.03	32.43	32.64	0.7283	0.7290	4265	2825.0	4301	2858.0	3991	2809.0	+6.9	+7.9	+0.6	+1.7
0.05	32.07	32.39	0.7330	0.7345	6868	4541.0	6985	4629.0	6567	4629.0	+4.6	+6.4	—1.9	0.0
0.07	31.72	32.14	0.7376	0.7399	9250	6370.0	9470	6539.0	9080	6403.0	+1.9	+4.3	—0.5	+2.1
0.10	31.24	31.79	0.7443	0.7473	12730	8806.0	13150	9132.0	12730	8988.0	0.0	+3.3	—2.0	+1.6
0.13	30.78	31.46	0.7512	0.7548	16280	11240.0	16960	11770.0	16260	11490.0	+0.1	+4.3	—2.2	+2.4
0.16	30.34	31.13	0.7578	0.7617	19550	13620.0	20550	14390.0	19660	13900.0	—0.6	+4.5	—2.0	+3.5
0.20	29.79	30.72	0.7663	0.7704	23700	16670.0	25200	17820.0	24030	16980.0	—1.4	+4.9	—2.0	+4.9
0.24	29.27	30.33	0.7746	0.7792	27740	19666.0	29810	21260.0	28200	19950.0	—1.7	+5.7	—1.9	+6.6
0.27	....	30.06	.....	0.7859	.....	21650.0	.....	23780.0	.....	22110.0	....	....	—2.0	+7.6

Judging from these figures, there can hardly be any question that the density of the solvent and not that of the solution is to be used in computing π by the hydrostatic method.

RUTGERS COLLEGE, May, 1898.

METHOD OF PREPARING A STRICTLY NEUTRAL AMMONIUM CITRATE SOLUTION.

BY A. D. COOK.

Received June 8, 1898.

FOR the benefit of many analytical chemists who are engaged in fertilizer work and for the purpose of securing uniformity in results, I respectfully submit the following pertaining to the neutrality and preparation of the chemical reagent "ammonium citrate."

This reagent has caused more trouble than all the other reagents required in fertilizer work, and yet it is an extremely easy matter to get a strictly neutral reaction.

The method adopted by the Association of Official Agricultural Chemists does not state the most essential fact in the preparation of this reagent, and the one which, if universally adopted, would overcome many obstacles in its preparation.

The failure to obtain a strictly neutral solution of ammonium citrate has caused great discrepancy in results among chemists who have analyzed the same material. I refer more particularly to the analysis of concentrated phosphates where there is a large per cent. of available phosphoric acid. The total phosphoric acid running as high as fifty per cent., the insoluble eleven per cent., making the available thirty-nine per cent. In the chemical laboratory at this station, where from 800 to 1000 samples of commercial fertilizers are analyzed annually, I have had ample opportunity to try different methods and to compare results obtained by chemists working with different solutions of ammonium citrate. It has been pointed out by fellow-workers in this field that a strictly neutral solution may be obtained by allowing the solution to stand after ammonia has been added to the citric acid and the proper dilution made. I have found that the practicability of this procedure depends upon the temperature of the solution. If vigorous stirring is neglected the solution will be slightly alkaline. Vigorous stirring, thus causing

heat by chemical action, will generate sufficient heat to drive off the excess of ammonia, and this is the main point to observe in securing its neutrality.

This reagent is made up as follows in this laboratory: 740 grams of commercial citric acid are carefully weighed out and placed in a four-liter graduate containing 1900 cc. of ten per cent. ammonium hydroxide. With a suitable glass rod the citric acid is thoroughly and vigorously stirred until the citric acid has all dissolved. Distilled water is now added until the meniscus reads 4000 cc. The solution is again stirred and carefully transferred to a large porcelain evaporating dish. The solution is allowed to stand over night and in the morning large oval crystals are noticeable on the sides of the four-liter graduate, and invariably the solution when tested for neutrality will be found strictly neutral. If the solution is not vigorously stirred sufficient heat will not be evolved to drive off the excess of ammonia, and when tested will be found to be slightly alkaline, but by resorting to vigorous stirring, a strictly neutral reaction will be obtained. The solution, after being transferred to the reagent bottle, is brought to the required temperature, 20° C., and distilled water added until the specific gravity is 1.09. On testing the neutrality of this solution, both with coralline and cochineal as indicators, it will be found unnecessary to alter its neutrality in the least degree, the solution being strictly neutral.

THE ASSAY OF TELLURIDE ORES.

By Charles H. Fulton.

Received June 8, 1898.

THE growing importance of telluride ores and the fact of their relative difficulty of assay in contrast with other ores, has led to this work. The object of the work was to determine where the difficulty and losses lay, and if possible to remedy these defects of the assay by proper methods and precautions.

Ore No. 1 is a telluride ore, having a gangue, mainly of quartz. A very small amount of pyrite is also present.

Ore No. 2 is a very rich telluride from Cripple Creek, Colorado, containing considerable pyrite. The gangue is siliceous.

Both ores were finely crushed, No. 1 crushed to 100-mesh, and No. 2 to 150-mesh, to insure an even sample. The crucible assay was tried on these ores with various modifications of the charge as regards the amount of litharge present. All assays on ore No. 1 were made on one assay ton of ore. The assays on ore No. 2 were made on one-fifth assay ton.

The charges for ore No. 1 were as follows, except that the litharge increased from one assay ton to six assay tons in the series :

1 assay ton ore.
1 assay ton litharge.
½ assay ton silica.
1 assay ton soda.
10 grams borax glass.
2 grams argol.
Salt cover.

The amount of silver in the ore is very small, and was disregarded in the assays. Twenty milligrams of silver foil were added to each crucible assay to give a larger button in cupellation and to avoid subsequent inquartation. Four iron nails were also added to each assay to desulphurize and give a malleable button.

The lead buttons ranged in weight from twenty to forty-eight grams, the increase in weight being due to the increasing litharge. All buttons were fairly malleable and were cupelled directly, even the larger buttons, without previous rescorification. The cupellation was conducted at a low heat, with feathers of litharge.

The assays show a regular increase of gold as the litharge increases, with the exception of B and B_6 and ranged from 5.60 milligrams to 5.78 milligrams. A further increase of litharge showed no better result. (See Table I.)

The slags from these crucible assays were ground up and mixed with one assay ton of litharge and two grams of argol, and fused. The resulting lead button was cupelled with the addition of ten milligrams of silver to give a button which could be parted.

The results of correction of the crucible assay show that con-

TABLE I.—SHOWING EFFECT OF INCREASING LITHARGE. ORE NO. 1.

Number of assay.	Amount of litharge	Amount of argol.	Character of slag.	Character of lead button.	Weight of lead button.	Amount of gold.	Gold recovered from crucible slag	Gold recovered from cupel.	Total amount of gold recovered.	Percentage recovered from crucible slag.	Percentage recovered from cupel.	Total percentage recovered.	Amount of gold in corrected assay.
	Assay tons.	Grams.			Grams.	Milligrams.	Milligram.	Milligram.	Milligram.	Per cent.	Per cent.	Per cent.	Milligrams.
A	1	2	black glassy	malleable	20	5.60	0.03	0.09	0.12	0.52	0.55	2.07	5.72
B	2	2	" "	brittle	37	5.52	0.16	0.02	0.18	2.76	0.18	2.94	5.70
B_0	2	2	" "	"	47	5.69	0.03	0.01	0.04	0.52	0.09	0.61	5.64
C	4	2	green glassy	"	32	5.67	0.05	0.01	0.06	0.86	0.09	0.95	5.73
C_0	4	2	" "	"	30	5.65	0.08	0.02	0.10	1.38	0.18	1.56	5.75
D	6	2	" "	malleable	48	5.72	0.06	0.01	0.07	1.03	0.09	1.12	5.79
D_0	6	2	" "	"	45	5.78	0.06	0.01	0.07	1.03	0.09	1.12	5.85
				Averages,		5.65	0.068	0.013	0.09	1.16	0.12	1.48	5.74

These assays were run with iron nails to desulphurize.

siderable gold is retained in the slag. The assays which contain the least amount of litharge retain the most gold. The average correction was 0.068 milligram, which is equivalent to 1.16 per cent. The highest corrected assay was taken as 100. This loss of gold in the crucible slag is much greater than that in ordinary ore assays.

The cupels were also ground up and mixed with one assay ton of litharge, one and a half assay tons of borax glass, one assay ton of soda, and two grams of argol. Silver was added to the fusion.

The amount of gold recovered from the cupel is small, only 0.013 milligram, equivalent to 0.12 per cent.

It is also to be noted that the corrected assays increase with the greater quantity of litharge, as well as the uncorrected assays, which shows that part of the loss is due to volatilization.

Table II shows the effect of increasing the litharge on a rich telluride. The charges for this ore were as follows, except as before, for the varying litharge: One-fifth assay ton ore, two assay tons litharge, one assay ton soda, one gram argol. The ore had considerable reducing power, and one gram of argol was found to be sufficient to give the right-sized button.

The crucible slags were remelted and the resulting lead buttons cupelled. The actual loss of gold in slags for this ore was higher than for No. 1, although the percentage loss decreases. The loss in the cupel being small, it was neglected in this case. The silver contents of this ore were determined, but no correction for the loss of silver in slags and cupels was made.

When the button resulting from the fusion of a telluride ore was brittle, it was usually deemed necessary to rescorify it before cupellation. The button resulting from telluride fusions is usually brittle and scorification is almost always resorted to. A set of assays were run on ores No. 1 and No. 2 to determine whether this is of advantage. These sets were run, as the previous ones, with increasing litharge, but no nails were added to desulphurize. All the buttons were rescorified, some with the addition of test-lead.

Tables III and IV show the results of these sets. The gold is considerably lower when the buttons are rescorified, and also it is evident that the loss takes place during the scorification.

TABLE II.—SHOWING EFFECT OF INCREASING LITHARGE ON A RICH TELLURIDE. ORE NO. 2.

Number of assay.	Amount of litharge.	Amount of ore.	Amount of argol.	Character of slag.	Character of lead button.	Weight of lead button.	Amount of gold.	Gold recovered from crucible slag.	Percentage recovered from crucible slag.	Amount of gold in corrected assay.
	Assay tons.	Assay ton.	Gram.			Grams.	Milligrams.	Milligram.	Per cent.	Milligrams.
1	2		1	green glassy	fairly malleable	20	89.10	0.22	1.21	90.20
2	4		1	" "	" "	26	90.50	0.08	0.31	90.90
3	4		1	" "	" "	48	90.26	0.10	0.55	90.36
4	6		1	" "	malleable	28	90.30	0.09	0.49	90.75
					Averages,		90.04	0.09	0.45	90.55

TABLE III.—SHOWING EFFECT OF RESCORIFICATION OF LEAD BUTTON. ORE NO. 1.

Number of assay.	Amount of lith-arge.	Weight of lead button.	Weight after re-scorification.	Amount of gold.	Gold recovered from crucible slag.	Gold recovered from scorification slag.	Gold recovered from cupel.	Total amount of gold recovered.	Percentage recovered from crucible slag.	Percentage recovered from scorification slag.	Percentage recovered from cupel.	Total percentage recovered.	Amount of gold in corrected assay.
	Assay tons.	Grams.	Grams.	Milligrams.	Milligram.	Milligram.	Milligram.	Milligram.	Per cent.	Per cent.	Per cent.	Per cent.	Milligrams.
E	1	17	8	5.32	0.10	0.16	trace	0.26	1.72	2.76	trace	4.84	5.58
F	2	22	14	5.62	0.06	0.04	0.01	0.11	1.03	0.70	0.18	1.91	5.73
G	4	30	18	5.64	0.06	0.04	0.01	0.11	1.03	0.70	0.18	1.91	5.75
H	6	40	14	5.50	0.08	0.05	trace	0.11	1.38	0.52	trace	1.90	5.61
H_0	6	39	14	5.54	0.09	0.04	trace	0.13	1.55	0.70	trace	2.20	5.67
I	8	75	24	5.58	0.07	....	....	....	1.20	....	....	....	5.65
		Averages,		5.54	0.08	0.038	....	0.11	1.31	0.65	....	1.98	5.77

TABLE IV.—SHOWING EFFECT OF RESCORIFICATION OF LEAD BUTTON, RICH TELLURIDE. ORE NO. 2.

Number of assay.	Amount of litharge.	Amount of ore.	Amount of argol.	Character of lead button.	Weight of lead button.	Weight after rescorification.	Amount of gold.	Gold recovered from crux slag.	Corrected assay.
	Assay tons.	Assay ton.			Grams.	Grams.	Milligrams.	Milligram.	Milligrams.
10	4	1/2	none	malleable	68	29	89.30	....	....
11	4	1/2	"	"	54	26	89.60	....	....
12	6	1/2	"	"	76	24	88.50	0.20	88.70
						Averages,	89.13		

These assays were run with niter and iron nails to desulphurize.

This loss is partly in the scorification slag and partly by volatilization. The crucible slags, cupels, and scorification slags were remelted and the buttons cupelled. The loss in the crucible slag is a little higher than in the first set (Table I).

The average amount of gold recovered from the scorification slag is 0.038 milligram, equivalent to 0.65 per cent. The amount recovered from the cupel is very small and less than in Table I.

The assays run on the rich telluride, with rescorification, point to the same conclusion (Table IV). This set of assays was run with niter and iron nails to increase the oxidizing action and to desulphurize. This loss of gold during rescorification is much greater in tellurides than in ordinary ores. With the latter it usually amounts to no more than a trace. The average result, by direct cupellation, is always higher than that obtained when the buttons are first rescorified.

A charge with potassium cyanide was run on ore No. 1. Ore, one assay ton; potassium cyanide, two assay tons; litharge, one assay ton; salt cover and silver. This gave gold 5.40, which is much lower than the results of assays run by the ordinary charges.

The following are the average results obtained from the four sets of assays:

ORE NO. 1.

Average uncorrected assay, when cupelled directly, 5.65 milligrams.

Average corrected assay, when cupelled directly, 5.74 milligrams.

Average uncorrected assay, when button is rescorified, 5.54 milligrams.

Average corrected assay, when button is rescorified, 5.67 milligrams.

Average loss of gold in crucible slag, 0.075 milligram.

Average loss of gold in per cent., 1.23 per cent.

Average loss in cupel, when cupelled directly, 0.013 milligram.

Average loss in cupel, in per cent., 0.12 per cent.

Average loss in scorification slag, 0.038 milligram.

Average loss in per cent., 0.65 per cent.
Total gold recovered when cupelled directly, 0.09 milligram.
Total gold recovered in per cent., 1.48 per cent.
Total gold recovered when rescorified, 0.11 milligram.
Total gold recovered in per cent., 1.98 per cent.

ORE NO. 2.

Average uncorrected assay, cupelled directly, 90.04 milligrams.
Average corrected assay, cupelled directly, 90.55 milligrams.
Average uncorrected assay, when rescorified, 89.13 milligrams.
Average loss of gold in crucible slag, 0.09 milligram.
Average loss of gold in per cent., 0.45 per cent.

A set of assays was also run in which the heat of the fire and time in fire was varied, to determine whether these factors had any influence on the result obtained. The fires were varied from a red to a white heat and the time from thirty minutes to one hour. The difference in results was not appreciable, and a good, moderately hot fire, with from forty to fifty minutes in the furnace, gave the best results. Cupellation, however, should be carried on at a low heat.

SCORIFICATION ASSAYS.

Both ores, Nos. 1 and 2, were run by scorification with very variable results, but uniformly lower than the crucible assay.

Ore No. 1 was assayed by the following charge:

Ore, one-fifth assay ton.
Test-lead, seventy grams.
Borax glass, one-half gram.
Litharge cover, twenty grams.

This gave gold = 4.30 milligrams. (Crucible assay ran 5.62 milligrams.) In the next charge the test-lead was increased to eighty grams. Otherwise charge was the same.

This gave gold = 4.80 ounces.

Then to further increase the ratio of ore to test-lead these charges were run in duplicate.

No. 1.	No. 2.
Ore, one-tenth assay ton.	Ore, one-tenth assay ton.
Test-lead, fifty grams.	Test-lead, sixty grams.
Borax glass, one-half gram.	Borax glass, one-half gram.
Litharge cover, twenty grams.	Litharge cover, twenty grams.

No. 1 gave gold, 4.20 and 4.00 milligrams, respectively.

No. 2 gave gold, 5.00 and 5.40 milligrams, respectively.

The heat was kept low throughout.

More assays were run by various charges, but invariably gave low results. A great drawback to the method is the large amount of test-lead which must be used, giving a button too large to be cupelled easily. The litharge cover seems of advantage, but also tends to increase the size of the lead button by protecting the lead from scorification.

Ore No. 2 was run by the following charge:

Ore, one-tenth assay ton.
Test-lead, fifty grams.
Litharge cover, twenty grams.
Borax glass, one-half gram.

This gave gold, 74.80 ounces (crucible assay, 90.20 ounces).

The test-lead was increased to sixty grams, giving 78.70 milligrams gold.

The scorification slags were ground up and assayed:

No. 1 gave 0.42 milligram = five and six-tenths per cent. of gold.

No. 1 gave 0.38 milligram gold.

This makes corrected result per assay ton on No. 1 = 79.0 milligrams.

This makes corrected result per assay ton on No. 2 = 81.8 milligrams.

This shows the corrected assay by scorification still away below the ordinary crucible assay. The loss of gold in scorification slag is very great, but evidently a still greater loss takes place by volatilization.

These results readily show that the crucible assay is much the better for telluride ores.

CONCLUSIONS.

It is very evident that a large excess of litharge is necessary to obtain good results in assaying a telluride ore. The amount of litharge will vary with the richness of the ore, the proper proportion of litharge to ore being maintained in a rich telluride by decreasing the quantity of ore. A definite ratio of litharge to gold present in telluride ores might be established.

The loss of gold in the crucible slag is many times more than that in assaying ordinary ores, and with both low and high grade ores justifies the making of corrected assays where accuracy is required. The loss of gold by absorption in the cupel is not of much account.

Scorification of any kind is bad for a telluride ore, whether it be the direct scorification of the ore or the rescorification of brittle or large buttons.

The loss in cupelling a large or brittle button directly is much less than if it were first rescorified.

The amount of gold lost in the scorification slag when scorifying the ore directly is very great, amounting to five and six-tenths per cent.

The highest uncorrected result also gives the highest corrected result, showing that loss takes place by volatilization. The loss of gold in a rich telluride is greater than in a low grade ore, but the percentage loss decreases with the richness of the ore.

In general, the crucible assay is best by far for telluride ores. The fire should be moderately hot, the length of time from forty to fifty minutes. The assay should be so conducted as to give a button of good size, from twenty to twenty-eight grams, which can be cupelled directly. The cupellation should be done at a low heat with crystals of litharge forming on the cupel. When the assay is to be accurate, the crucible slag should be remelted and the first result corrected. The cupel correction can be disregarded.

Mr. F. C. Smith publishes an article in the *Trans. Am. Inst. Min. Eng.*, **26**, 485, on "The Occurrence and Behavior of Tellurium in Gold Ores, etc.," which is partly devoted to the assay of telluride ores. His experiments prove that the crucible

assay is the better for telluride ores, and that the loss of gold in the assay is very great if the charge is not properly made up as regards the amount of litharge present. He does not locate the loss or make corrected assays.

In the discussion of Mr. Smith's paper, Mr. Wm. P. Jenney states that he believes an oxidizing charge with a small quantity of ore would be beneficial. The excess of litharge, of course, has an oxidizing action, but to try this point further the assays in Table IV were made by the following charge:

Ore, one-fifth assay ton.
Litharge, four assay ton.
Soda, one and a half assay tons.
Silica, one assay ton.
Six loops of wire.
Twenty grams of niter.

The wire acted as the reducing agent with the sulphur. The buttons were good and malleable, but on cupellation gave no better results than charges with litharge alone.

ON THE LINDO-GLADDING METHOD OF DETERMINING POTASH.

By A. L. Winton[1] and H. J. Wheeler.[2]

Received June 15, 1898.

IN view of certain criticisms of the Lindo-Gladding method of potash determination which have appeared of late, notably those by Vogel and Haefcke,[3] we were appointed a committee by the Association of Official Agricultural Chemists of the United States to prepare an article setting forth certain work bearing upon the points involved.

At the regular meeting of the Association in Washington in 1890, Frear and Sweetser[4] called attention to certain comparative determinations made by them, which indicated that the use of sodium chloride was unnecessary. The mean difference in

[1] Chemist Conn. Agricultural Experiment Station and Reporter on methods of potash determination for the Association of Official Agricultural Chemists for the years 1896 and 1897.

[2] Chemist R. I. Agricultural Experiment Station and Reporter on methods of potash determination for the Association of Official Agricultural Chemists for the years 1894 and 1895.

[3] Die landw. Versuch-Stationen 47 (1896), pp. 112-117.

[4] U. S. Dept. of Agr., Div. of Chem., Bull. 28 (1890), p. 73.

the results with and without sodium chloride amounted to but 0.04 per cent., and in but two cases out of fifty was the difference over 0.10 per cent. In 1891, Winton[1] investigated the matter thoroughly and in tests conducted with commercial potash salts and twenty-four mixed fertilizers, showed that the results with and without the addition of sodium chloride were practically identical.[2] The same line of study was further pursued in 1892 by Payne,[3] in cooperation with twenty-two chemists in seventeen different laboratories, working with a variety of substances. As a result of these investigations by the Association the use of sodium chloride was discontinued.[4] This was done not because inaccurate results were obtained by its use, but in order to abbreviate the method by striking out a cumbersome and useless detail.

Notwithstanding the fact that it had already been abundantly shown that there was practically no difference in the results obtained with and without the use of sodium chloride, Breyer and Schweitzer[5] asserted that its use was a source of error. Their claim that it was unnecessary was merely a reiteration of what had already been shown by the work of the Association.

Aside from the undesirability of employing sodium chloride the only unfavorable criticism of the Lindo-Gladding method worthy of note, which has appeared, is based upon the assumption that a considerable error is introduced through double decomposition resulting from contact of the ammonium chloride wash solution with potassium platinichloride. Breyer and Schweitzer[6] and N. Robinson[7] mention errors thus arising and the two former chemists claim that the amount of the same is considerable. Their conclusions in this respect are based chiefly upon the amount of potassium chloride said to have been recovered from the ammonium chloride wash solution which had already been employed in washing precipitates of potassium platinichloride. It does not appear, however, that blank determinations were made for the purpose of ascertaining the amount

[1] U. S. Dept. of Agr., Div. of Chem., Bull. 31 (1891), pp. 148–150.
[2] Compare Fresenius' *Ztschr. anal. chem.*, 16, 63.
[3] U. S. Dept. of Agr., Div. of Chem., Bull. 35 (1892), pp. 58–61.
[4] U. S. Dept. of Agr., Div. of Chem., Bull. 35 (1892), pp. 197, 198.
[5] *J. Anal. Appl. Chem.*, 6, (*1892*), 477.
[6] *J. Anal. Appl. Chem.*, 6, (*1892*), 474–477.
[7] This Journal, 16, (*1894*), pp. 366, 367.

of potash, if any, contained in the ammonium carbonate, ammonium oxalate, and in the seven grams of barium hydroxide and other reagents employed in the recovery of the potash. In view of the fact that considerable amounts of potash are frequently present in certain so-called chemically pure reagents employed in potash determinations,[1] it would appear that a large part of the potash, said by Breyer and Schweitzer to have been recovered from the wash solution, may have been derived from their reagents. It is obvious, therefore, that their results instead of serving as a proper basis for the criticism of a method, are themselves open to serious criticism.

The ammonium chloride wash solution experimented with by Breyer and Schweitzer was the same as that employed by the Association, the preparation of which is described in a succeeding foot-note. That a great amount of double decomposition may result with this solution, under exaggerated conditions, has been shown by the work of the Association[2] during 1894 and 1895. This fact alone furnishes no suitable basis for the condemnation of the method, provided the amount of error arising in the ordinary course of analysis is practically insignificant.

During the years 1894[3] and 1895[4] one of us (H. J. W.) conducted comparative determinations to learn whether washing with ammonium chloride solution, according to the Lindo-Gladding method, introduced an appreciable error. The analytical work was carried out with the cooperation of analysts of the Association of Official Agricultural Chemists of the United States, nine taking part during the first year and ten during the second year, no two of them working in the same laboratory or with the same reagents.

In 1894 portions of four grams each of pure potassium chloride were made up to one liter with water and twenty-five cc. of this solution, representing one-tenth gram of the salt, were taken for each determination. As the salt contained a small amount of water, which, in the portions sent to the different analysts, varied from 0.06 to 0.16 per cent., the results have in

[1] U. S. Dept. of Agr., Div. of Chem., Bull. 43 (1894), pp. 21, 22; also Bull. 47 (1895), pp. 16, 17; and Bull. 49 (1896), pp. 30–32.

[2] U. S. Dept. of Agr., Div. of Chem., Bull. 43 (1894), pp. 23, 24; and Bull. 47 (1895), p. 22.

[3] U. S. Dept. of Agr., Div. of Chem., Bull. 43, pp. 17–25.

[4] U. S. Dept. of Agr., Div. of Chem., Bull. 47, pp. 14–23.

each case been calculated to correspond with one-tenth gram of the dry material (see Table I).

TABLE I.

COMPARISON OF RESULTS ON PURE POTASSIUM CHLORIDE BY THE LINDO-GLADDING METHOD AND BY THE METHOD OF WASHING WITH ALCOHOL ONLY (1894). ONE-TENTH OF A GRAM OF POTASSIUM CHLORIDE TAKEN IN EACH DETERMINATION.

Analyst.	Potassium platinichloride washed with alcohol only. Potassium chloride found.	Potassium platinichloride washed with alcohol and ammonium chloride solution, (Lindo-Gladding method). Potassium chloride found.	Results by washing with ammonium chloride are more (+) or less (−) than those without.
	Gram.	Gram.	Gram.
W. A. Powers, Illinois Station.....	0.10053	0.10134	
	0.10114	0.10159	
Average	0.10084	0.10147	+0.00063
F. P. Veitch, Maryland College	0.09867	0.09864	—0.00003
J. B. Lindsey, Massachusetts Station.	0.10112	0.10082	
	0.10066	0.10097	
	0.10066	0.10060	
		0.10005	
Average.....	0.10082	0.10061	—0.00021
W. L. Rossman, Michigan Station..	0.09957	0.09974	
	0.09951	0.09956	
	0.09957	0.09971	
	0.09933	0.09965	
Average	0.09950	0.09967	+0.00017
J. P. Street, New Jersey Station	0.09838	0.09807	
	0.09868	0.09838	
	0.09871		
Average	0.09859	0.09823	—0.00036
B. L. Hartwell, Rhode Island Station	0.09960	0.09898	
	0.09954	0.09913	
		0.09934	
Average	0.09957	0.09915	—0.00042
K. P. McElroy, U. S. Dept. of Agr .	0.10000	0.10015	
	0.10012	0.10040	
Average	0.10006	0.10028	+0.00022
R. de Roode, West Virginia Station.	0.09996	0.09993	—0.00003

The determinations carried out in 1895 were made on solu-

tions of fifty cc. each, containing from three-tenths to one gram of pure potassium chloride, thus exposing to the action of the ammonium chloride solution three to ten times as much potassium platinichloride as in the preceding year.

The salt used was from a new lot containing uniformly 0.45 per cent. of moisture; the weights of potassium chloride taken, as given in Table II, represent, however, the dry salt.

In the determinations of both years, each solution of the pure salt was evaporated to a paste with an excess of platinum solution. The residue, after cooling, was stirred for twenty minutes with thirty cc. of eighty per cent. alcohol (sp. gr. 0.8645) and the liquid decanted on a weighed Gooch crucible. The washing was further continued by decantation, using ten cc. portions of alcohol and stirring for from two to three minutes after each addition.

In some cases the salt, without further washing, was dried at 100° C. and weighed; in others it was first washed with six portions of ammonium chloride solution[1] of ten cc. each and finally with eighty per cent. alcohol, according to the Lindo-Gladding method.

Blank determinations were made by both methods on the reagents. From the analytical data secured in these determinations, which were given in full in *loc. cit.*, Tables I and II have been prepared.

In calculating the results the total weight of potassium platinichloride obtained in each determination was first corrected by deducting the average weight obtained by the same analyst from the reagents.

For the conversion of potassium platinichloride to potassium chloride the factor 0.3069[2] was employed for reasons stated later.

A careful study of the results given in the tables will make it evident that the potassium platinichloride was very slightly, if at all, acted upon by the ammonium chloride solution. Finkener[3] found that a saturated solution of ammonium chloride at 22° C., when in contact with finely divided potassium platini-

[1] A solution of 100 grams of ammonium chloride in 500 cc. of water, which had been shaken for from six to eight hours with five to ten grams of pulverized potassium platinichloride, allowed to settle over night, and filtered.

[2] Platinum 195.0, potassium 39.11, chlorine 35.45.

[3] Pogg. *Ann.*, 129, 627.

TABLE II.

COMPARISON OF RESULTS ON PURE POTASSIUM CHLORIDE BY THE LINDO-GLADDING METHOD AND BY THE METHOD OF WASHING WITH ALCOHOL ONLY (1895).

Analyst.	Potassium platinichloride washed with alcohol only.			Potassium platinichloride washed with alcohol and ammonium chloride solution (Lindo-Gladding method).		
	Potassium chloride taken.	Potassium chloride found.	Potassium chloride, error.	Potassium chloride taken.	Potassium chloride found.	Potassium chloride, error.
	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.
W. A. Powers, Illinois Station.....				0.3976	0.3954	—0.0022
				0.3872	0.3871	—0.0001
B. L. Hartwell, Rhode Island Station[1].	0.4776	0.4780	+0.0004	0.4534	0.4532	—0.0002
	0.4458	0.4463	+0.0005	0.4799	0.4797	—0.0002
	0.4665	0.4668	+0.0003			
	0.5437	0.5442	+0.0005			
G. Wm. Gray, West Virginia Station..	0.5114	0.5110	—0.0004	0.5028	0.5002	—0.0026
				0.5080	0.5049	—0.0031
F. P. Veitch, Maryland College	0.5004	0.5002	—0.0002	0.5043	0.5058	+0.0015
	0.5666	0.5685	+0.0019	0.5149	0.5163	+0.0014
	0.5005	0.5027	+0.0022			
W. H. Allen, North Carolina Station...				0.2987	0.2989	+0.0002
				0.2987	0.2988	+0.0001
				0.2987	0.2985	—0.0002

[1] These results have been corrected for an error in the original table.

TABLE II.—(*Continued*).

COMPARISON OF RESULTS ON PURE POTASSIUM CHLORIDE BY THE LINDO-GLADDING METHOD AND BY THE METHOD OF WASHING WITH ALCOHOL ONLY (1895).

Analyst.	Potassium platinichloride washed with alcohol only.			Potassium platinichloride washed with alcohol and ammonium chloride solution (Lindo-Gladding method).		
	Potassium chloride taken.	Potassium chloride found.	Potassium chloride, error.	Potassium chloride taken.	Potassium chloride found.	Potassium chloride, error.
	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.
J. B. Lindsey, Massachusetts Station...	0.4978	0.4987	+0.0009	0.4978	0.4985	+0.0007
	0.4978	0.4986	+0.0008	0.4978	0.4979	+0.0001
W. G. Brown, U. S. Dept. of Agr.....	0.6479	0.6506	+0.0027	0.5550	0.5559	+0.0009
	0.5731	0.5749	+0.0018	0.5557	0.5560	+0.0003
	0.4796	0.4798	+0.0002			
J. P. Street, New Jersey Station	0.4978	0.4981	+0.0003	0.4978	0.4996	+0.0018
	0.4978	0.4977	−0.0001	0.4978	0.4993	+0.0015
				0.4978	0.4985	+0.0007
E. P. Stone, New Hampshire Station ..	0.5022	0.5043	+0.0021	0.5022	0.5043	+0.0021
	0.5883	0.5902	+0.0019	0.5883	0.5902	+0.0019
A. L. Winton, Connecticut Station.....	0.4500	0.4508	+0.0008	0.5011	0.5010	−0.0001
	0.5004	0.5013	+0.0009			
	0.5331	0.5338	+0.0007			
	0.5310	0.5313	+0.0003			

chloride for one hour, decomposed but 0.27 per cent. of the latter. Since the Lindo-Gladding method, at least as applied to the potash salts, secures the double salt in a granular condition, which according to Finkener is not so rapidly acted on, and since operating with a Gooch crucible the ammonium chloride solution is not in contact with the double salt longer than two or three minutes, errors from this source would not be expected to be and, as numerous results show, are not appreciable. There are few if any analytical methods where the precipitate is absolutely insoluble in the wash liquid and it is absurd to discriminate against the Lindo-Gladding method for theoretical reasons which have no practical significance.

Breyer and Schweitzer state that it is very "doubtful whether the method of Lindo-Gladding is a simplification of Fresenius' method." At all events, it should be stated that the members of the Association after having given both methods an extended trial find the latter decidedly shorter.

Breyer and Schweitzer state that potassium platinichloride obtained by them by the Lindo-Gladding method contained impurities, notably magnesium and calcium sulphates, but as they give no figures it is to be assumed that the amounts present were not determinable.

If the potash exists as chloride, and chlorides of sodium, magnesium and calcium are the only soluble impurities, evaporation with platinum solution and washing with alcohol should yield pure potassium platinichloride, the salts of chloroplatinic acid with the other bases being readily soluble in alcohol. Were this not true neither the Lindo-Gladding nor the Stassfurt method would be practicable.

If, however, the bases mentioned are combined wholly or in part with sulphuric acid, the potassium platinichloride, obtained by the Lindo-Gladding method, is usually, after the first washing with alcohol, contaminated with magnesium and calcium sulphates, subsequent washing with ammonium chloride solution being depended upon to remove these impurities.

Magnesium sulphate is readily soluble in the ammonium chloride solution. Even when a very considerable amount is present, the first addition of the reagent removes almost instantly the greater part of it. Calcium sulphate does not dissolve so

readily but it is contained only in small amount in the potash manure salts on sale in the United States and the treatment with ammonium chloride solution effectually removes both this salt and the magnesium sulphate.

That this is true is shown by the figures obtained by one of us (A. L. W.) which are given in Table III. The results calculated from the weights of potassium platinichloride (together with many others equally accurate obtained by seven American chemists) were reported to the Association of Official Agricultural Chemists in 1896,[1] but those calculated from the weights of metallic platinum are here given for the first time.

The materials used were chemically pure potassium sulphate, which had been ignited until all water was removed, and three mixtures representing the water-soluble impurities contained in "sulphate of potash (ninety per cent.)," "sulphate of potash and magnesia," and "kainit." The solutions for analysis, representing half gram portions of the commercial potash salts named, were prepared by mixing weighed portions of the pure salt with the corresponding amounts of the mixtures of impurities, dissolved in each case in twenty-five cc. of water. The determinations of potash in these solutions presented the same analytical difficulties as would have been encountered in the analysis of the real commercial salts, but the exact amount of potash present was in each case known and the results obtained could be compared with theory.[2]

The Lindo-Gladding method of the Association[3] was strictly followed except in the case of kainit solution, which was evaporated directly with platinum solution, without previous separation of lime, as was originally directed by Gladding.[4] The potassium platinichloride was weighed on Gooch crucibles, reduced in hydrogen, washed with hot water, ignited, and finally

[1] U. S. Dept. of Agr., Div. of Chem., Bull. 49, pp. 27–38.

[2] At the present time only four Stassfurt products are used in any considerable amount for agricultural purposes in the United States; viz., "ninety per cent. sulphate of potash," or "high grade sulphate of potash," "sulphate of potash and magnesia," or "low grade sulphate of potash," "kainit," and "eighty per cent. muriate of potash." Each of these is reasonably uniform in composition, containing, in addition to the potash salts, a certain proportion of chlorides and sulphates of soda, magnesia, and lime. In making the mixtures above described, the average composition of the commercial salts, as published by the German Kali Works, was followed.

[3] U. S. Dept. of Agr., Div. of Chem., Bull. 46, p. 23.

[4] U. S. Dept. of Agr., Div. of Chem., Bull. 7, p. 41.

weighed as metallic platinum, all of which was accomplished without transfer.

The small amounts of potash in the "impurities" were determined by careful analysis and calculated as potassium sulphate.

The conversion factors employed were: K_2PtCl_6 to K_2SO_4, 0.3587; and Pt to K_2SO_4, 0.8937. These were derived from the following atomic weights: Pt = 195.0, K = 39.11, Cl = 35.45, S = 32.06, O = 16.0.

The factors which have been commonly used in potash determinations (0.3056 for converting K_2PtCl_6 to KCl, 0.3570 to K_2SO_4 and 0.19308 to K_2O) are those based on an atomic weight of platinum long since abandoned. Fresenius[1] found in some determinations made on pure potassium chloride, shortly after the now accepted atomic weight of platinum was determined by Seubert[2] that the factor 0.3056 gave results nearer theory than the factor derived from the later atomic weights. But it has been shown by one of us (A. L. W.)[3] that when platinum solution is added to a concentrated solution of the potash salt, as was done by Fresenius, much of the potassium platinichloride separates out at once as a finely divided precipitate, which, examined under the microscope, may be seen to consist of radiating crystals, enclosing numerous globular cavities containing liquid. Part of the enclosed liquid is slowly driven off at 100°, more at 130°, and more still at 160° C. As Fresenius dried at 130°, the water was presumably only partially removed and for this reason the lower factor gave the best results.

Winton has further shown, however, that when the solution of the potash salt is so dilute that the addition of the platinum solution either forms no immediate precipitate or one that dissolves on heating, the potassium platinichloride deposits slowly, on evaporation, in the form of coarsely granular crystals which appear under the microscope to be almost entirely free from enclosed liquid and which dry as completely on heating three hours at 100°, as when heated for many hours at 130° and 160° C. When the salt is obtained by this latter method, as was the case in all the determinations of Tables I, II, and III, the factors

[1] *Ztschr. anal. Chem.*, 21, 238.
[2] *Ann. Chem.* (Liebig), 207, 1.
[3] This Journal, 17, 453.

based on the latest atomic weights give satisfactory results. The fact that the results (given in Table III) obtained by the Lindo-Gladding method and calculated by the revised factor, agree closely with those calculated from the weight of the platinum and with theory, is of itself a strong indication of the purity of the potassium platinichloride and the perfection of the process. It is only in the case of methods which yield an impure double salt that it is necessary to resort to the unscientific procedure of retaining incorrect factors in order to compensate for errors of the method.

Vogel and Haefcke,[1] as their first point against the Lindo-Gladding method, claim that the addition of sodium chloride is unnecessary and is liable to prove a source of error. This intended criticism was made in 1896, five years after the matter was first considered by the Association and three years after the Association had ceased to employ it, a fact which they might have ascertained had they consulted the published records of the proceedings of the Association.

Again, Vogel and Haefcke, after calling attention to the well-known fact of the double decomposition which results when potassium platinichloride is acted upon by ammonium chloride, further add that proof is lacking to show that the ammonium chloride, even after having been brought in contact with potassium platinichloride, is not capable of effecting still further double decomposition. Assuming that such further action results to a degree which practically interferes with the accuracy of the method, they find therein another point against it. In fact two years before this theoretical criticism was published, the Association had shown that the wash solution was capable, under greatly exaggerated conditions of treatment, of further effecting a considerable amount of double decomposition; but at the same time, as has already been shown, it was proved that in actual analytical work the amount of error thus introduced was practically so small as to furnish no valid objection to the method. Vogel and Haefcke could have learned these facts also before their criticisms appeared, had they consulted the published records of the association whose official methods they were discussing. It must be conceded that upon theoretical

[1] Die landw. Versuchs-Stationen, 47, (1896), pp. 115-116.

TABLE III.

RESULTS BY THE LINDO-GLADDING METHOD ON MIXTURES REPRESENTING "SULPHATE OF POTASH NINETY PER CENT.," "SULPHATE OF POTASH AND MAGNESIA," AND "KAINIT."

Taken impurities corresponding to 0.5 gram of	Potassium sulphate, pure salt, taken.	Potassium sulphate, in impurities, taken.	Potassium sulphate, total taken.	Potassium platinichloride found.	Platinum found.	Results calculated from weight potassium platinichloride.		Results calculated from weight platinum.	
						Potassium sulphate found.	Potassium sulphate, error.	Potassium sulphate found.	Potassium sulphate, error.
	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.
"Sulphate of potash 90 per cent."	0.4042	0.0002	0.4044	1.1248	0.4523	0.4035	—0.0009	0.4042	—0.0002
	0.4121	0.0002	0.4123	1.1483	0.4615	0.4119	—0.0004	0.4124	+0.0001
	0.4110	0.0002	0.4112	1.1448	0.4591	0.4106	—0.0006	0.4103	—0.0009
"Sulphate of potash and magnesia"	0.3040	0.0003	0.3043	0.8470	0.3408	0.3038	—0.0005	0.3046	+0.0003
	0.2686	0.0003	0.2689	0.7490	0.3017	0.2687	—0.0002	0.2696	+0.0007
	0.2566	0.0003	0.2569	0.7136	0.2866	0.2560	—0.0009	0.2561	—0.0008
"Kainit"	0.1387	0.0005	0.1392	0.3860	0.1547	0.1385	—0.0007	0.1383	—0.0009
	0.1727	0.0005	0.1732	0.4807	0.1922	0.1724	—0.0008	0.1718	—0.0014

grounds only, many valuable and reliable methods of analysis would have to be discarded if the solvent action of the wash liquids, regardless of the degree of solubility, were the sole basis for such a procedure.

The variation in the time employed in washing the potassium platinichloride due to unequal rapidity of filtration and the size of the crystals to be washed, are also urged by Vogel and Haefcke as logical objections to the method. However, by the use of the Gooch crucible and by precipitating the potassium platinichloride from dilute solutions by which large crystals are obtained, it must be obvious and in fact it has been shown by abundant analytical data, that these objections hold only from a theoretical, and not from a practical, standpoint.

Vogel and Haefcke still further assert, based upon assumption or upon the previously mentioned statements of Breyer and Schweitzer, that the potassium platinichloride obtained by the Lindo-Gladding method contains many impurities and therefore that it is not advisable to weigh the double salt as such. However, as has been shown by the results in Table III, the potassium platinichloride obtained by the Lindo-Gladding method even in the presence of such impurities as are in commercial ninety per cent. sulphate of potash and sulphate of potash and magnesia, as well as in kainit, is practically pure and the results accord as closely as could be desired with those obtained by reduction and weighing the metallic platinum.

From what has been said above it will be seen that Vogel and Haefcke were not well informed as to the work of the Association nor in relation to the status of the method in vogue when their unfavorable criticisms were made; furthermore, they present no analytical data of their own in support of their assumptions and in the main the points which they sought to make were but a reiteration of the previous unfavorable criticisms of Breyer and Schweitzer, which have been shown by abundant data to have been, so far as practical considerations go, utterly unfounded.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF LAFAYETTE COLLEGE.]

A NEW VOLUMETRIC METHOD FOR THE DETERMINATION OF COPPER.

BY RICHARD K. MEADE.

Received May 2, 1898.

THE average analyst is often deterred from the use of a volumetric method by the necessity of making and standardizing a special solution. In many cases it takes nearly as much time to ascertain the strength of the required solution as it does to make the analysis itself, and the standardization and analysis together render the volumetric method frequently as slow, if not slower, and vastly more troublesome than the gravimetric determination.

Volumetric analysis, therefore, becomes more and more an ideal method of quantitative determination as it approaches the requirement of a single standard solution, capable of having its strength accurately determined by simple means, giving a single, definite, clear end-reaction.

In iron and steel laboratories permanganate is fast coming to the front as a help to rapid analysis. Iron, phosphorus, manganese, sulphur (Payne's iodine solution is prepared by adding standard permanganate to potassium iodide) and calcium can all be quickly determined by the use of one standard solution. While it may never be possible to supplant other standard solutions by permanganate, still the sphere of its usefulness is a large one and is constantly enlarging.

For a year or more I have been experimenting upon a new method for the determination of copper by permanganate, which seems to possess many points of superiority over the old one of reduction by grape sugar. In general it is as follows: The copper is brought into solution as a sulphate, either by dissolving it in sulphuric acid or evaporation of its solution with sulphuric acid. The greater part of the free acid is neutralized by ammonia, the solution warmed, sulphurous acid added until the solution smells strongly of the reagent, and then a slight excess of ammonium or potassium thiocyanate.[1] The copper

[1] Rivot: *Compt. rend.*, **38**, 868; and Busse: *Ztschr. anal. Chem.*, *1878*, 55.

is immediately precipitated as cuprous thiocyanate. Stirring and warming renders the precipitate heavy and easily handled. The solution is filtered through asbestos, using the pump, and well washed. The precipitate and filter are thrown into the beaker in which the precipitation was made and heated with a solution of caustic soda or caustic potash. Double substitution takes place. Hydrated cuprous oxide and potassium or sodium thiocyanate result.

$$2CuSCN + 2KOH = Cu_2(OH)_2 + 2KSCN.$$

The oxide is filtered on asbestos and washed well with hot water. The precipitate and filter are again placed in the same beaker and an excess of ferric chloride or ferric sulphate (free from nitric acid, free chlorine or ferrous salts) together with a little dilute sulphuric acid added. The copper oxide reduces a corresponding amount of iron from the ferric to the ferrous condition.

$$Cu_2O + Fe_2Cl_6 + 2HCl = 2CuCl_2 + 2FeCl_2 + H_2O.$$

The beaker is warmed and stirred until all the copper oxide is dissolved. The solution is then poured through a perforated platinum disk and the asbestos which stays behind upon it washed with water, to which has been added a little sulphuric acid and a little ferric chloride or sulphate. The solution is then titrated with permanganate. The iron equivalent to the permanganate used multiplied by 1.125 gives the weight of copper in the sample.

Instead of sulphurous acid, ammonium or sodium bisulphite may be used to reduce the copper. A solution of equal weights of sodium bisulphite and potassium thiocyanate answers well as a reagent for the precipitation of the metal. Since copper is the only metal precipitated by an alkaline thiocyanate from an acid solution, the presence of arsenic, antimony, bismuth, zinc, and other materials which render the electrolytic, the cyanide, and the iodine method inaccurate, will not affect the results.

The caustic alkali solution, used to convert the cuprous thiocyanate into cuprous hydroxide, must not be too strong or some of the metal will go into solution, coloring the liquid blue. I have used about a half normal solution of caustic potash,

made by dissolving twenty-eight grams of the salt in a liter of water. Either ferric sulphate or ferric chloride may be used to dissolve the cuprous oxide. The former is probably the safest, but the latter appears to dissolve the precipitate the more readily of the two.

As a test of the accuracy of the method four grams of pure electrolytic copper were dissolved in nitric acid and the solution evaporated with sulphuric acid until the nitric acid was expelled. The solution was cooled and diluted to one liter. The copper contained in fifty cc. was then determined electrolytically with the following result:

	Gram.
1	0.2003
2	0.2003
3	0.2000
4	0.1997
Average	0.2001

The copper in fifty cc. was next determined by the thiocyanate-permanganate method outlined above. The permanganate solution used was made by dissolving 5.02 grams of pure crystallized potassium permanganate in water and diluting after standing twenty-four hours to two liters. Its strength was determined by titration against iron wire and against ferrous ammonium sulphate.

Against ferrous ammonium sulphate:

	Gram iron.
1. One cc.	= 0.004455
2. One cc.	= 0.004456

Against iron wire:

	Gram iron.
3. One cc.	= 0.004460
4. One cc.	= 0.004449
Average one cc.	= 0.004455

One cc. = 0.004455 × 1.125 = 0.005012 gram copper.

Below are the results on fifty cc. of the copper solution containing 0.2001 gram copper by the thiocyanate-permanganate method:

No.	Permanganate. cc.	Copper. Gram.
1	39.6	0.1985
2	39.5	0.1980
3	39.6	0.1985
4	39.7	0.1990
5	40.0	0.2004
6	39.8	0.1995

In determinations numbers 1, 5, and 6, ferric chloride was used to dissolve the cuprous oxide; in numbers 2, 3, and 4, ferric sulphate was used.

As a further and more practical test of the method, the copper in some samples of copper ore was carefully determined by the electrolytic, and then by the thiocyanate-permanganate method. Below are the comparative results:

Sample.	Weight of sample. Gram.	Permanganate. cc.	Copper by thiocyanate-permanganate method. Per cent.	Copper by electrolytic method. Per cent.
1. Chalcopyrite I	1.0	39.6	19.85	19.95
2. "	1.0	39.3	19.70	19.86
3. Chalcopyrite II	2.0	24.6	6.16	6.37
4. "	2.0	24.8	6.21	6.30
5. Malachite	1.0	72.2	36.19	36.10
6. "	1.0	72.2	36.19	36.15
7. Tetrahedrite	1.0	42.0	21.05	21.06
8. "	1.0	41.7	20.90	21.18

It will be seen by the above results that the method is accurate enough for ordinary commercial purposes. In spite of its three filtrations, the method is quite rapid. Not counting the time required for the solution of the ore, duplicate analyses can be easily made in from a half to three-quarters of an hour.

In the writer's opinion the process is superior to both the iodine and the cyanide method. It requires the use of no rapidly changing solutions, but one which every analyst has on hand nearly all the time. The end-reaction is clear, distinct, and familiar to all chemists. The method is applicable to any ore, matte or alloys. It is as rapid as the cyanide, except in certain cases favorable to the latter, and more rapid than the iodine method. Finally, not the least of its points of advantage is that it is more accurate than either of the two.

EASTON, PA., May 2, 1898.

ON THE SEGREGATION OF CARBON IN A PIECE OF BOILER PLATE.

By Henry Fay and Henry P. Talbot.

Received June 15, 1898.

A PIECE of steel has recently come into our hands for examination which, by its unusual and striking properties, strongly emphasizes the necessity for careful heat treatment. The specimen was a circular steel plate, one-fourth inch in thickness and about three feet in diameter, and was intended for use as the head-piece of a pressure cylinder to hold carbon dioxide.

Unfortunately, the complete history of the piece was not obtainable, but it is known that after its receipt from the manufacturers the plate was twice annealed and was then to be punched into a cup-shaped cylinder head. On flanging, however, the plate cracked around the entire bend, which was made about four inches from the circumference, the cracks being fully one-sixteenth inch deep and more than an inch long.

Samples for analysis were taken from the edge of the plate and from the center, and test pieces were also taken from both portions for examination as to tensile strength and elongation. The specifications called for a mild steel containing about 0.30 per cent. carbon.

The results of the analysis are tabulated below:

	Outer portion. Per cent.	Center portion. Per cent.
Phosphorus	0.005	0.006
	0.004	0.008
	0.003	0.005
	0.006	0.005
	....	0.004
Sulphur	0.033	0.050
	0.042	0.050
	0.033	0.040
Manganese	0.36	0.38
	0.37	0.38
Carbon	0.130	0.087
	0.036	0.070
	0.110	0.124
	0.156	0.060
	0.067	0.090
	0.080	0.030
	0.076	0.091
	....	0.070
	....	0.100

It will be noted that, with the exception of the carbon and sulphur, the percentages represent about normal values for a steel which would be suitable for the purpose named.

The carbon determinations, on the other hand, exhibit the most astonishing variations, ranging between 0.036 and 0.156 per cent. in the outer portions, and 0.060 and 0.124 per cent. in the center. A thorough examination of chemicals and apparatus, and repeated blank analyses, made it certain that errors from these sources were eliminated, and it only remained to conclude that the varying percentages represented inequalities in the composition of the material under analysis.

For the physical tests, made by Professor E. F. Miller, of the Massachusetts Institute of Technology, three test pieces were taken, one of which was from the flange where the crack showed, the others from the unbent portion. The specimen from the flange was straightened by being heated to a bright cherry-red, and the tensile strength was determined in the usual way. The fracture did not take place at the point where the crack occurred, as one might expect.

The following results were obtained:

	1.	2.	3. Test-piece from flange.
Dimensions of cross-section	2″ × 0.3850″	2″ × 0.3850″	2″ × 0.380″
Tensile strength	44,690	44,670	45,960
Elongation	28.1	....	....

It will be seen that the material would probably have been rejected on account of low tensile strength, not to mention the fact that the carbon determinations had shown the material to be far from homogeneous.

The results of the physical tests, however, threw no light upon the cause of the inequalities in the carbon contents of the steel, but upon etching a small, roughly polished portion with dilute nitric acid (sp. gr. 1.13), the fact was at once demonstrated that the steel was badly crystallized.

Other portions of the plate were then cut and carefully polished with various grades of emery and finally with rouge. This polishing served to etch the samples sufficiently to permit of an examination with the microscope which, in turn, showed the carbon to be unevenly distributed throughout the mass.

Upon etching the surface a trifle more deeply, in relief, with dilute nitric acid (sp. gr. 1.13), the grains of ferrite were very clearly brought out, as can be seen in the accompanying cut (Fig. 1), which represents the crystals in their natural size.

A similar examination of the edge of the plate made it evident that the crystallization had penetrated only part way through the mass. A glance at Fig. 2 will show the depth to which the crystallization had extended.

The test pieces which were subjected to the tensile tests also show this superficial crystalline structure in a peculiar way. Instead of pulling uniformly and breaking sharply, the crystalline layers slipped along on the non-crystalline portion and the surface was more or less pitted as a result of the depression of some of the crystals and the elevation of others, caused by the breaking apart of the separate crystals. The uniformity with which the crystalline structure has penetrated the metal, and this slipping of the two layers would seem to suggest that the plate was the "composition metal" of trade, or had been made by the process of "piling." Without a knowledge of the early history of the plate it is impossible to speak conclusively upon this point.

Sauveur[1] has shown experimentally that (*a*) "a slow and undisturbed cooling from a temperature x or higher, produces crystallization; (*b*) undisturbed cooling from an initial temperature lower than x is not accompanied by crystallization; (*c*) the higher the initial temperature from which the steel is allowed to cool undisturbed, the larger the grain for a given composition." Again, Osmond,[2] in discussing the heat treatment of steels, states that "in proportion as the temperature of annealing is elevated, the polyhedra of ferrite increases in size."

In the specimen under examination the grains of ferrite are not only visible to the unaided eye but some of them are of unusual size, measuring in transverse section as much as 1.5 × 1 cm., and there is further evidence of the faulty heat treatment in the microstructure which shows an uneven distribution of the pearlyte. There is therefore very little doubt that this specimen of steel has been subjected, during the annealing process, to a

[1] *Trans. Am. Inst. Min. Eng.*, 22, 546.
[2] *Ibid.*, 22, 255.

Fig. 1. Showing grains of Ferrite. Natural size.

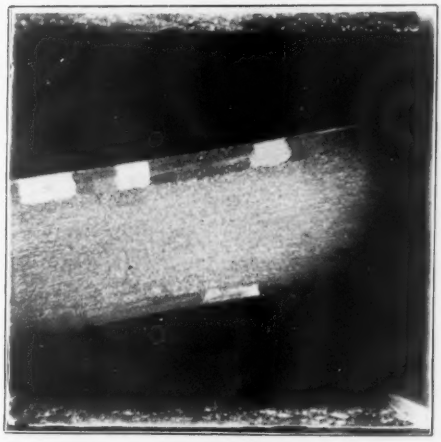


Fig. 2. Side view. Showing depth of crystallization.

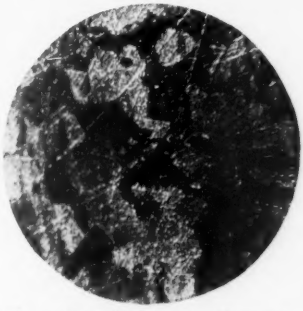


Fig. 3. Magnified about 30 diameters.

temperature materially higher than that required, and has been allowed to cool extremely slowly. It is more than probable that the crystallization took place during the annealing process rather than during the manufacture of the plate, for the reason that cooling of the plate after rolling would necessarily be more rapid than after annealing, and to produce crystals of such size would require slow and undisturbed cooling.

The fact that the steel was overheated was further attested by the unusual thickness of the scale.

With respect to the variations in the percentage of carbon, it is safe to assume that the high temperature burned out a portion of the carbon and what remained had segregated during the process of crystallization, particles of carbon being distinctly visible on the polished surface with the help of a hand magnifying glass. That such a segregation of carbon may take place during crystallization is well demonstrated in a piece of open-hearth steel (kindly sent to us by Mr. Kreuzpointer of the Pennsylvania Railroad Laboratory of Tests), which had broken through the bottom of the furnace and over which more than three hundred heats had been made. That the polished and etched surface shows a marked similarity to that of the steel for the pressure cylinder is evident from Fig. 3, which shows well-marked crystals of ferrite, and the portion standing in relief is the segregated carbon, which can be seen in the sample with the unaided eye.

As has already been stated, the sharp line of demarcation between the crystalline exterior and non-crystalline interior, as shown in Fig. 2, suggests a "composition metal" and there is no definite evidence to disprove this. It may not, however, be out of place to ask the question: whether, if the heating of the plate in the furnace, although too strong, had yet been sufficient to effect it but partially, and if it had been at once transferred to the annealing oven where it could cool slowly, a similar result with respect to crystallization might not be within the bounds of possibility. Whether then the finished piece was originally composition metal or had been produced by the heating alone, there can be no doubt that it was ruined by the heat treatment.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
June, 1896.

THE MINERAL CONSTITUENTS OF THE TUBERCLE BACILLI.

By E. A. de Schweinitz and Marion Dorset.

Received April 14, 1898.

IN August, 1895,[1] the writers published the results of some analyses showing the composition of the tubercle bacilli when grown upon different media. Depending upon the character of the media used, the amount of ash varied from two to four per cent. It seemed desirable to make a careful analysis of the ash in order to see which of the mineral constituents of the animal body would be most largely utilized by the germ and consequently necessary for its satisfactory development. The bacilli used for this work had been grown upon neutral beef broth containing one per cent. of peptone, one-half per cent. salt, and seven per cent. glycerol. The cultures, after heating in order to kill the germs, were filtered and washed well with boiling water. The washed bacilli were then dried over sulphuric acid, finely powdered, and thoroughly extracted with pure ether and ninety-eight per cent. alcohol. After the last extraction the bacilli were again dried and ignited at a low red heat until practically all the carbon had been burned. The ash, which was almost pure white in color, was dried to a constant weight at 100° C. The total ash available for analysis was 1.453 grams. Examination showed that sulphates, chlorides, and carbonates were not present in the ash. The method used for the determination of the constituents of the ash were those prescribed for the analyses of the ash of plants. The results calculated upon the dry ash were as follows:

	Per cent.
Na_2O	13.62
K_2O	6.35
CaO	12.64
MgO	11.55
C and Si	0.57
P_2O_5	55.23

The high percentage of phosphorus pentoxide and the absence of other acid radicals in this ash are very noticeable. While it is probable that some of the chlorides and sulphates

[1] This Journal, 17, 605.

may have been washed out of the germ in the process of preparing it for analysis, no chlorides were present in the germs after washing; the fact that the amount of phosphoric acid obtained in the ash is slightly lower than the total amount of phosphoric acid obtained from the whole germ, would indicate that chlorides and sulphates are practically of no importance in the composition of the germ, while their presence in the culture media in minute quantity appears to be necessary for the satisfactory development of the germ. Chlorides and sulphates if dissolved out would have been present probably as cell contents rather than as part of the germ.

Ash analyses of comparatively few germs have been made, and the only ones which give data that may be reported here are the analyses made by Cramer,[1] who found that the composition of the ash of the cholera germs varied greatly, depending upon the quantity of sodium chloride and sodium phosphate that were used in the preparation of the media. In normal media the results were as follows:

	Per cent.
Cl	17.02
P_2O_5	20.48
SO_4	8.55
K	6.32
Na	32.06
Ca	0.98
Mg	trace

If the amount of sodium chloride in the media was increased, the percentage of chlorine in the ash was more than doubled, while the percentage of SO_4 found was reduced to one per cent., and the percentage of P_2O_5 was largely diminished, being reduced to 9.64 per cent. When sodium phosphate was added to the media the percentage of chlorine was found to be 9.99 per cent., the percentage of P_2O_5 34.30 per cent., SO_4 2.24 per cent., of potassium 4.97 per cent., of sodium 31.83 per cent., of calcium 1.29 per cent., of magnesium 0.12 per cent. These results differ greatly from those found in the examination of the ash of the tubercle bacilli. As noted above, the media used for the growth of these latter germs was a normal material containing one-half per cent. of salt, but without the addition of any

[1] *Archiv. für Hygiene*, 28, No. 1.

phosphates or other salts. Consequently the high percentage of phosphorus pentoxide can be attributed only to the fact that phosphorus as well as the calcium and magnesium are absolutely necessary for the development of the tubercle bacilli, and were derived by it from these elements as normally present in the media.

In arrested cases of tuberculosis in animals, we often find hard, gritty, calcareous nodules. These nodules in healed tuberculosis contain tubercle bacilli. In other cases of healed tuberculosis where calcareous nodules are not present no bacilli as a rule are found. It is easy to trace a very close connection between these nodules in healed tuberculosis, and the composition of the ash of the germ.

The high percentage of fat contained in the body of the tubercle bacilli, which we have noticed in previous papers, in conjunction with this high percentage of calcium and magnesium phosphate in the ash, give grounds for some interesting speculation. Phosphates and cod-liver oil are two materials always strongly recommended in cases of tuberculosis. As the germs of this disease seem to demand a large quantity of food containing phosphorus and also rich in fat, it is but a fair supposition that in giving the drugs above mentioned, we are supplying to the animal body those constituents which are very important for its proper nourishment, the supply of which is constantly being levied upon by the germs of the disease. The question might be asked whether in this method of treatment we are not really feeding the bacilli rather than the individual. But just as an exhausted soil can be made valuable by the addition of constituents which are deficient, so we may assume that the administration of specific materials containing the elements that the germ has utilized, should act in a similar way in increasing the vitality in the animal body. These of course are speculations, based, however, on certain known data. We trust that a still further study which is in progress, including the albuminoid constituents of the tubercle bacilli, may throw some light upon their development and chemical action in the animal body.

BIOCHEMIC LABORATORY,
WASHINGTON, D. C.

THE SPECIFIC GRAVITY OF SODIUM CHLORIDE SOLUTIONS.

By H. C. Hahn.

Received April 8, 1898.

THE specific gravity and expansion by heat of salt solutions have not received the attention of chemists and physicists to the extent which they deserve. The data for common salt, for example, are only sufficient for technical purposes.

To the best known determinations of the specific gravity of sodium chloride solutions belong those of J. A. Bischof, G. Karsten, and G. T. Gerlach. Since the publication by Bischof in 1810, so many improvements in physical apparatus and more exact determinations of certain necessary factors, have been made, that we need not take his determinations into consideration. Those of G. Karsten, in 1846, show extraordinary diligence. His method is to weigh a glass ball in a salt solution, which stands in a large vessel full of water to be heated gradually. In this method there is danger of the one beam of the balance getting warmer than the other by the ascending current of heated air from the lamp and the hot water. Nevertheless, his method is the best, if modified as explained below. Further, Karsten did not determine the coefficient of expansion of his glass ball, but used the one determined by Munke, which is not admissible in very exact determinations. He does not state that the degrees of the mercurial thermometer were corrected to those of the air thermometer; nor that in calculating the weight of the weights and the glass ball in the vacuum, he took into consideration the amount of water and carbon dioxide in the air. The determinations by Gerlach[1] are the best; but some of the same and some other objections have to be raised against them. He did not determine the coefficient of expansion of his pycnometer, but used the one of Dulong and Petit. Reducing the weights to the vacuum, he assumed the atmosphere to have been saturated with water, which very probably was not the case. He compared the different specific gravities with that of water of 15°, instead of with that of 4°. He did not correct the degrees of the mercurial thermometer, and

[1] Spec. Gewichte der gebräuchlichsten Salzlösungen von verschiedenen Concentrationsgraden, Freiberg, 1859.

instead of calculating a formula for each series of determinations, he calculated the specific gravities of the solutions of certain percentages by interpolation from the two nearest determinations. Some of these defects may yet be corrected. This I have done and give in the following the details with different methods to eliminate errors.

Sodium chloride. Per cent.	Sp. gr. at 15° of mercurial thermometer compared with water of 15°.	Sp. gr. at 15.08° of air thermometer compared with water of 4°.
	1.	2.
0	1.000 00	0.999 12
5	1.036 24	1.035 33
10	1.073 35	1.072 40
15	1.111 46	1.110 48
20	1.151 07	1.150 05
25	1.192 28	1.191 23
Saturated at 15°	1.204 33	1.203 27

For the numbers in column 1 different formulas may be calculated, according to the number of figures used. To the values for five, ten, twenty, and twenty-five per cent. corresponds the formula:

$$s = 0.999,03 + 0.007,203\,p + 0.000,009,4\,p^2 + 0.000,000,4\,p^3,$$

when s signifies the specific gravity and p the per cent. of sodium chloride. But the values for naught and fifteen per cent., as calculated by this formula, would be: 0.999,03 and 1.110,54, which are slightly erroneous.

A formula calculated according to the method of least squares, with the use of the 4th power is:

$$s = 0.999,12 + 0.007,072,54\,p + 0.000,024,206,76\,p^3,$$

which gives the values of column 3. The sum of least squares is 0.000,000,175.

3.	4.
0.999,12	0.999,12
1.035,09	1.035,12
1.072,26	1.072,30
1.110,65	1.110,69
1.150,25	1.150,27
1.191,06	1.191,04

The differences of the observed and calculated values are larger than of those obtained by the foregoing formula. I calculated

therefore another one with the use of the 5th and 6th power:

$$s = 0.999,12 + 0.007,079,96\,p + 0.000,023,844,27\,p^2 + 0.000,000,001,002,876\,p^3,$$

which gives the numbers in column 4, with the sum of least squares = 0.000,000,177,6, which is no improvement on the former formula.

As a specimen of such calculations, I give here the items for the last formula:

s.

$$\begin{aligned}
0.999,12 &= a \\
1.035,33 &= a + 5x + 5^2y + 5^3z \\
1.072,40 &= a + 10x + 10^2y + 10^3z \\
1.110,48 &= a + 15x + 15^2y + 15^3z \\
1.150,05 &= a + 20x + 20^2y + 20^3z \\
1.191,23 &= a + 25x + 25^2y + 25^3z
\end{aligned}$$

p^2.	p^3.	p^4.	p^5.	p^6.
25	125	625	3,125	15,625
100	1,000	10,000	100,000	1,100,000
225	3,375	50,625	759,375	11,390,625
400	8,000	160,000	3,200,000	64,000,000
625	15,625	390,625	9,765,625	244,140,625
1375	28,125	611,975	13,828,125	320,546,875

$p(s-a)$.	$p^2(s-a)$.	$p^3(s-a)$.
0.181,05	0.905,25	4.526,25
0.732,80	7.328,00	73.280,00
1.670,40	25.056,00	375.840,00
3.018,60	60.372,00	1,207.440,00
4.802,75	120.068,70	3,001.718,00
10.405,60	213.729,95	4,622.804,25

According to the method of least squares, we have the following equations:

$$\begin{aligned}
p\,(s-a) &= p^2x + p^3y + p^4z \\
p^2(s-a) &= p^3x + p^4y + p^5z \\
p^3(s-a) &= p^4x + p^5y + p^6z
\end{aligned}$$

Substituting into these equations the values obtained above, they become:

$$\begin{aligned}
10.405,60 &= 1,375x + 28,125y + 611,975z \\
213.729,95 &= 28,125x + 611,975y + 13,828,125z \\
4,662.804,25 &= 611,975x + 13,828,125y + 320,546,875z
\end{aligned}$$

which further developed give the last formula mentioned above.

Another method is to calculate series of differences of the numbers of the main series. The method is only applicable if the values of p rise or fall in an arithmetical proportion.

The series 2 above gives the following series of differences:

0.999,12				
1.035,33	3621			
1.072,40	3707	86		
1.110,48	3808	105	15	Average.
1.150,05	3957	149	48	25
1.191,23	4118	161	12	

Since each arithmetical series of the nth degree gives n, and only n series of differences, we know at once to which degree the desired formula belongs.

In reconstructing the main series and the series of differences backward, from the first member of the series, *i. e.*, 3621, 86, 25, we get the values given below in column 5.

If s is the first member of the main series, ds that of the first difference series, d_2s that of the second, etc., the nth member of the main series is:

$$S_n = s + (n-1)\,ds + \frac{(n-1)(n-2)}{1 \times 2}\,d_2s + \frac{(n-1)(n-2)(n-3)}{1 \times 2 \times 3}\,d_3s.$$

The sixth member of the main series is therefore:

$$S_6 = s + 5ds + \frac{5 \times 4}{1 \times 2}\,d_2s + \frac{5 \times 4 \times 3}{1 \times 2 \times 3}\,d_3s.$$

If we substitute in this equation for ds the value 3620, the second member of the main series will be found to be too small by 1; the third by 2; the fourth by 3. If for d_2s we substitute 85, the third member will be too small by 1; the fourth by 3; the fifth by 6, and the sixth by 10. A similar result is obtained if for d_3s we substitute 24. By diminishing ds (= 3621) by 1, we get numbers which correspond best with those observed, with the sum of least squares equal to 0.000,000,000,54. They are given in column 6.

5.	6.			
0.999,12	0.999,12			
1.035,33	1.035,32	3620		
1.072,40	1.072,38	3706	86	
1.110,58	1,110,55	3817	111	25
1.150,12	1.150,08	3953	136	25
1.191,27	1.191,22	4114	161	25

To calculate a formula for the values of column 6, we have the following points to consider. The first member of the formula will be: 0.999,12, and the fourth equal to $\frac{0.00025}{1 \times 2 \times 3 \times 5^3}$ = 0.000,000,333,333. Any two values of the main series will give the second and third members of the formula, thus:

$$s = 0.999,12 + 0.007,1707\,p + 0.000,0122\,p^2 + 0.000,000,333,333\,p^3.$$

It is generally believed that by the method of least squares formulas corresponding best with the observed values are obtained; but we see that the method of series of differences may give a better result. The above tables and formulas are not convenient in practice, in which generally the specific gravity is known and the per cent. of sodium chloride is sought. It is therefore necessary to construct another formula, corresponding to the reversed condition, for which purpose any four values of column 6 should be sufficient. But it was found impossible to construct out of four, or all six of the numbers, a formula of the third degree which would give exactly the values of column 6.

I calculated therefore from the last formula the per cent. of sodium chloride in a solution whose specific gravity is a little less than 1.00, and likewise the per cent. of sodium chloride in a solution whose specific gravity is a little more than 1.00; and similarly for the solutions of 1.05, 1.10, 1.15, 1.20, 1.25 specific gravities, and found by interpolation the per cent. corresponding to the desired specific gravity. For example:

		Specific gravity.
	0.1 sodium chloride	= 0.999,84
	0.2 " "	= 1.000,55
Difference	0.1 " "	= 0.000,71

Therefore 0.077,46 per cent. sodium chloride = 0.000,55 specific gravity.

$0.2 - 0.077{,}46 = 0.122{,}54$ per cent. sodium chloride solution has the specific gravity of 1.00.

In this way the values of column 7 were obtained.

Specific gravity.		7. Per cent. sodium chloride.				
1.00	=	0.122,54				
1.05	=	6.995,95	6.873,41			
1.10	=	13.633,77	6.637,82	0.235,59		
1.15	=	19.990,12	6.356,35	0.281,47	0.045,88	
1.20	=	26.040,00	6.049,88	0.306,46	0.025,00	0.020,88
1.25	=	31.777,53	5.737,73	0.312,35	0.005,88	0.019,12

It is seen at once that with a trifling change a formula of the fourth degree can be calculated, whose second and fourth members are preceded by a minus sign, because the first and third series of differences are diminishing from top to bottom, and whose fifth member is: $\frac{0.02 \times 20^4}{1 \times 2 \times 3 \times 4} = 133{,}333{,}333\cdot$

A minimum of changes is obtained if the third series of differences is made the following: 0.045,44, 0.025,44, 0.005,44, and hence we get the following main series:

8.				
0.122,485				
6.996,005	6.873,52			
13.633,715	6.637,71	0.235,81		
19.990,175	6.356,49	0.281,25	0.045,44	
26.039,945	6.049,77	0.306,69	0.025,44	0.02
31.777,585	5.737,64	0.312,13	0.005,44	0.02

from which the following formula is calculated:

$$\text{Per cent.} = 60.209{,}585 - 626.853{,}1s + 1067.352{,}667s^2 - 633.92s^3 + 133{,}333{,}333s^4,$$

which, if the specific gravity at 15.08° air thermometer is known exact to the fourth decimal, will give the per cent. of sodium chloride exact to 0.01.

Gerlach determined also the expansion by heat of different solutions of sodium chloride. I tried to find a formula for his values according to the method of least squares, with the help of the fifth power of the temperature; but the calculated values showed differences in the average of 0.000,33 (the largest was 0.000,62).

A main factor in determinations of specific gravity is the knowledge of the specific gravity of the air in the balance case, which depends on the barometric pressure, temperature, and its percentage of water and carbon dioxide. More exact than by calculation is the direct determination, which is made in the same manner as the determination of the specific gravity of the liquid itself. For this purpose I recommend the use of three solid gilded cylinders of pure aluminum of precisely the same weight. Cylinders are to be preferred to globes, and a metal is to be preferred to glass, because cylinders and metal acquire more quickly the temperature of the surrounding medium, and are more conveniently made of equal volume. Each cylinder should weigh at least twenty grams. Since the specific gravity of aluminum is 2.67, a cylinder of two cm. diameter and three cm. length weighs 25.16 grams in air, 9.42 grams in cold water, and 7.95 grams in a liquid of 1.25 specific gravity.

A balance, which indicates one-tenth milligram under a load of 25 grams, will indicate only about five-tenths to one milligram, if the cylinder to be weighed is immersed into a very heavy liquid, so that the weight, respectively loss of weight of a twenty-five gram cylinder in a liquid of 1.25 specific gravity, may be ascertained within the $\frac{0.001}{25} = 0.00004$ part of 1; therefore the specific gravity is correct within at least the fourth decimal.

Before gilding, a hook of platinum wire is fastened to the end of each cylinder. The exact equal weight being established, the cylinders are gilded. If the equality of the weight has been disturbed, it is restored by inverting the lighter cylinder for a short time again in the gold-bath.

After the weighing pans of the balance have been removed, a beaker with freshly distilled water is put under each end of the beam; and by the aid of thin platinum wire an aluminum cylinder is fastened on each of the hangers of the beam, so that the cylinders are immersed in the water. After a time sufficient for the cylinders to acquire the temperature of the water, and after ascertaining that the temperature of the latter is exactly the same in both beakers, it is observed whether the weights of the cylinders in water are equal or not. If there should be any slight difference, the lighter cylinder is transferred to the left side and

the difference of the weights made up by a piece of thin platinum wire, to be attached to the hanger of the left-hand beam. The same operation is repeated with the third cylinder, after the removal of the cylinder on the left-hand side.

If this is satisfactorily accomplished, the beakers with water are removed and, when the temperature of the room is nearly 0°, two tumblers are procured, with ground rims and ground covers, the latter each containing in the center a hole of about five-tenths cm. diameter, and near the rim a hole to admit a thermometer, which has a cylindrical vessel, and is graduated on the stem. The one tumbler is filled partly with fused calcium chloride and caustic lime or potash; the other is nearly filled with cold distilled water. The first tumbler is put under the hanger of the left beam, and the other under that of the right-hand beam. After a time, sufficient for the cylinders and the water to acquire the temperature of the surrounding air ($t°$), the weight is read off. It is:

x = the weight of each aluminum cylinder in grams.

y = the volume of each aluminum cylinder in cc.

z = difference of weights, if one is immersed in pure air, the other in pure water.

z_1 = the same, reduced to the vacuum.

a = specific gravity of pure water at $t°$ (air thermometer) and h barometric pressure.

b = specific gravity of dry air at $t°$ (air thermometer), and h barometric pressure.

b_1 = specific gravity of the air at $t°$ (air thermometer) in the balance case.

c = specific gravity of the gilded weights at $t°$ (platinum weights are to be preferred).

Then $$x + ay - z_1 = x + by,$$

or $$\frac{z_1}{a - b} = y \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Further $$z_1 = z + z\frac{b_1}{c}$$

or $$z_1 = \frac{z(c + b_1)}{c} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

If this value of z_1 is substituted in equation 1, we get: $y=\frac{z(c+b_1)}{c(a-b)}$. The same operation is repeated at about 25°, 50°, and 75°. In the latter two instances the temperatures of the water and air will, of course, differ considerably. From the values obtained, a table is calculated of the volumes of the aluminum cylinders for each degree of the air thermometer from 0° to 100°.

To ascertain the specific gravity of the air in the balance case at the time, when it is intended to determine the specific gravity of a liquid, the tumbler with pure water and thermometer is put under the left hanger of the balance, the cylinders hooked to the hangers of the beam, the one immersed in the water, the other in the air. After a time, sufficient for the water to have acquired the temperature of the air, the weight is read off. We have then:

$$x+ay-z_1=x+b_1y;\ \text{or}\ a-\frac{z(c+b_1)}{cy}=b_1.$$

Substituting for b_1 on the left side repeatedly the value $a-\frac{z(c+b_1)}{cy}$, we get:

$$a-\frac{z}{y}-\frac{za}{cy}+\frac{z^2(c+a)}{c^2y^2}-\frac{z^3(c+a)}{c^3y^3}+\frac{z^4(c+a)}{c^4y^4}-\frac{z^5}{c^5y^5}=b_1;$$

i. e., the specific gravity of the air, if that of the water is assumed to be 1.00. If $t°$ is not 4.1° C., b_1 has to be divided by a and the formula becomes:

$$1+\frac{\left(\frac{z^2(c+a)}{c^2y^2}+\frac{z^4(c+a)}{c^4y^4}\right)-\left(\frac{z}{y}+\frac{za}{cy}+\frac{z^3(c+a)}{c^3y^3}+\frac{z^5}{c^5y^5}\right)}{a}=b_1$$

The aluminum cylinder on the right hand is thence removed and the tumblers with the liquid to be examined, into which the third cylinder and a thermometer had already been immersed, is put in its place, the cylinder hooked to the hanger, and the weight ascertained.

If the specific gravity of a liquid at a high temperature is to be determined (*i. e.*, the expansion coefficient), a hole directly underneath the hanger of the right-hand beam passes through the upper and lower bottoms of the balance case and also through the table. Through this hole passes a platinum wire

connected with the one cylinder hanging in the beaker, containing the liquid, on a water-bath over a Bunsen burner.

When the liquid in the beaker has about the desired temperature, the lamp is extinguished and the weight of the cylinder ascertained.

Now the thermometer is read off again and the weight again ascertained. If the temperature has risen in the meantime the operation is repeated, till the weight is less than at the first reading. The averages of all temperatures and of all weights are taken and used for the computation.

A SHORT STUDY OF METHODS FOR THE ESTIMATION OF SULPHUR IN COAL.[1]

By G. L. Heath.

Received June 15, 1898.

AS manufacturer's requirements with regard to certain metallurgical processes become more exacting from year to year, the determination of sulphur in the fuel must become more important. The interest taken in this subject is evidenced by the appointment of the committee from the society who have just made their preliminary report. The writer has been led, as a matter of interest, to communicate some experimental work upon the determination of sulphur.

There has been a little controversy, or doubt, as to the relative accuracy of the two "sintering" or "ignition" methods in general use as compared with each other, or with the old method of fusion with sodium carbonate and potassium nitrate. It must be assumed and understood that the following work was done rather to study methods and show precautions necessary, than to obtain close check results. This remark explains a discrepancy in results on one coal of very high sulphur content, since the methods which will now be described as used by the writer, were purposely not modified to suit that special case.

I. THE "FUSION" METHOD.

This is so well given in the text-books with so little variation that full description is unnecessary.[2] Blair's modifications used.

[1] Read at the meeting of the New York Section, June 3, 1898.

[2] Blair's Analysis of Iron, *1888*, p. 245.

In our experience, much care must be taken to dehydrate, by evaporation with acid, the silicic acid which dissolves in the solution of the fused alkali. This renders the process too slow for technical work.

2. ESCHKA'S METHOD.[1]

a. One gram of powdered coal is intimately mixed with one gram of pure magnesium oxide and one-half gram sodium carbonate, and heated with the flame of a large (eight-ounce) alcohol lamp in a platinum dish of about 100 cc. capacity. A dish is much to be preferred to a narrow crucible, since it offers a better exposure of the coal to the air, and prevents excessive heat and dry distillation in the interior of the mass.

The mixture is frequently stirred with a platinum wire and the heat is raised very slowly, especially so with very soft coals. The flame, which is kept in motion and barely touches the dish at first until strong glowing has ceased, is increased gradually until, in fifteen minutes, the bottom of the dish is at a low red heat. When the carbon has burned away the mass is transferred to a No. 2 Griffin beaker and boiled five minutes with 100 cc. of distilled water and some oxidizing agent.

Fifteen cc. of saturated bromine water, as recommended by Mack and by Handy, is the purest and most efficient reagent to use, safer than the plan of adding ammonium nitrate during ignition. The hot liquid is then passed through a washed filter and the residue washed with hot water until the total volume is approximately 200 cc. The filtrate is then acidified strongly with hydrochloric acid, boiled until the free bromine is driven off, and sufficient hot solution of barium chloride added to insure the precipitation of all the sulphuric acid as barium sulphate, which is settled, filtered, and ignited.

b. Fresenius recommends that the ignited mixture be boiled directly in bromohydrochloric acid, which will dissolve all the sulphur in high coals, but loads the solution with salts and possibly silica.

c. The modification, recently published, involving the use of silver oxide, does not seem to offer any advantage whatever

[1] *Chem. News*, 21, 261; *J. Anal. Appl. Chem.*, 6, 611.

over the other methods using inexpensive material, and is not included in the table.

3. HUNDESHAGEN'S METHOD.[1]

It is a familiar fact that this modification differs from Eschka's only in the substitution of potassium carbonate for sodium carbonate. The advocate of the first salt claimed that sodium carbonate did not retain all the organic sulphur from certain Bohemian brown coals.

J. O. Handy,[2] of Pittsburg, presented tests from which he deduced a conclusion in opposition to that of Hundeshagen, but he does not appear to have tested the particular class of coals specified by the latter chemist. The writer has, accordingly, experimented with a variety of samples, including Bohemian brown coal, and has experimented also with a few variations in the details of procedure. Part of the foreign samples were procured from the Michigan College of Mines, and a fine specimen of the Bohemian article from Prof. Lattimore, of the University of Rochester.

The proximate analyses were carried out as usual with the author, according to Blair's[3] modification of Heinrich's method. Blank analyses for the sulphur in reagents were also carried through. This is the more necessary, as I have sometimes met with goods labelled by importers "strictly C. P.," which were rather impure.

An inquiry, in one case, elicited the statement from a clerk that his house labelled articles C. P. to fill orders for the highest grade, even if they were only a common grade on the market at the time. The American firm of Baker & Adamson, it is but just to state, has furnished the purest chemicals for fuel analysis that we could obtain anywhere.

4 AND 5. WILEY'S AND CARIUS' METHODS.

I have had no experience with the Wiley and Carius methods, which are not so much used, as such, in America.

6. WET METHOD OF CALVERT.

The "wet method" of Calvert[4] is useful for the scientific inves-

[1] *Chem. Ztg.*, **16**, 1070; also *J. Anal. Appl. Chem.*, **6**, 385.
[2] *J. Anal. Appl. Chem.*, **6**, 116.
[3] Blair's Analysis of Iron, *1888*, p. 243.
[4] *Chem. News*, **24**, 26; also Watts' Dictionary of Chemistry.

TABLE I.

PROXIMATE ANALYSES OF THE DOMESTIC AND FOREIGN COALS. SULPHUR INCLUDED IN FIGURES—NOT DEDUCTED FROM CARBON.

No.	Variety.	Special characteristics.	Locality.	Per cent. moisture at 105° C.	Per cent. volatile and combustible matter.	Per cent. fixed carbon.	Per cent. of ash.
1	Bituminous	clean lump	Ohio, U. S.	0.72	37.15	57.01	5.12
2	"	fine slack of	" "	0.78	30.72	54.92	13.58
3	Anthracite	clean lump	Penna., U. S.	2.47	3.00	88.80	5.73
4	"	" "	" "	2.95	3.23	86.95	6.87
5	Bituminous	" "	W. Va., U. S.	0.62	31.28	62.07	6.03
6	"	fine slack of	" "	0.75	29.64	62.75	6.86
7	Gray, soft	friable	Rhenish Prussia	2.72	23.03	6.41	67.84
8	Bituminous, soft	a little shaly	Pleasant Hill, Iowa, U. S.	1.26	43.72	45.65	9.37
8B	" "	weathered shaly sample	" " " "	1.85	42.90	45.97	9.28
9	Black, jet	lustrous, vitreous	Spain or Bohemia	2.83	38.70	49.46	9.01
10	Kerosene shale	grayish brown, woody pieces	N. S. Wales	0.07	82.05	5.81	2.07
11	Carmel	grayish	Hartley Vale, Blue Mts., N.S. Wales	0.07	81.37	5.32	13.24
12	Lignite	brown lump	Kosten, Bohemia	8.17	44.14	39.14	8.55

tigation of the forms in which the sulphur exists in fuel, but is unsuitable for technical work.

7. FAHLBERG-ILES PROCESS.[1]

The modified Fahlberg-Iles process of fusion with caustic potash in a silver crucible is correct, but is open to a strong objection, which does not affect either Eschka's or Hundeshagen's methods. It is necessary to heat slowly over an alcohol lamp to complete fusion, and the silica is thereby rendered soluble, but must be subsequently dehydrated by tedious evaporation. Accordingly, I have confined this work to the two most rapid technical methods, including a few results by complete fusion for comparison.

TABLE II.

EXPERIMENTAL SULPHUR DETERMINATIONS. PER CENT. OF SULPHUR FOUND.

No. of sample.	Treated in 100 cc. platinum dish.	Oxidized by bromine water. Eschka's method.	Hundeshagen's method.	Oxidized with hydrogen peroxide. Eschka's method.	Fusion method with sodium carbonate and potassium nitrate in crucible.
1	Ignited.....	1.375	1.364	1.372	....
2	"	2.203	2.197	....	....
3	"	0.529	0.551	0.545	....
4	"	....	0.530	0.521[2]	....
5	"	1.063	1.068	....	....
6	"	1.637	1.635	....	....
7	"	1.480	1.540	1.760(*c*)[3]	....
	"			1.690(*d*)	
8A	"	4.95	4.99	....	4.97(*e*)
	"		4.74		
8B[4]	"	4.76	4.69(*g*)	....	....
	"	(*h*)4.80	4.88(*m*)	....	4.89(*f*)
9	"	0.201	0.203	....	....
10	"	0.364	0.375	....	....
11A	"	0.43	0.41	....	....
11B	"	0.30	0.33	....	....
12	"	0.966	0.967	0.923	0.968
	"	(*h*)0.907		0.983(*d*)[3]	

[1] Furman's Manual of Assaying, *1895*, p. 88.
[2] Hundeshagen's method used in this case.
[3] Oxidized with sodium peroxide.
[4] This is sample 8A weathered by two years' exposure of the powder to air.

7(*c*). Two grams sodium peroxide added during the ignition.

7(*d*) and 12(*d*). Two grams of sodium peroxide added to the aqueous solution of the ignited residue, and boiled. The 7(*c*)(*d*) results are too high owing to dissolved silica.

8(*e*). The fused mass was directly dissolved in dilute acid, and then evaporated to dryness, taken up again with dilute hydrochloric acid, and filtered.

8(*f*). The fused mass was boiled with water only, and the solution filtered, then acidified with hydrochloric acid, and evaporated to dryness in order to dehydrate silica. (*g*). Ignited very quickly at strong heat in dish. (*h*). Ignited this quickly in crucible. See No. 8B, Hundeshagen's method, also No. 12. 8B, 11, and 12 were made with a compact variety of magnesium oxide, and in analysis 8B not quite all the sulphates could be extracted in five minutes boiling with water.

8(*m*). Ignited mass dissolved directly in bromohydrochloric acid.

From the foregoing experimental analyses in addition to regular work, considerable information has been secured concerning the effect of variation in the small details of the standard methods, and the precautions to be observed in their use, which might be summed up for discussion, as follows:

1. I cannot confirm the statement of Hundeshagen that Eschka's mixture does not retain all the sulphur from certain coals, and as far as my experience goes must agree with Handy's opinion with one qualification.

2. Rapid heating with magnesium oxide and alkaline carbonate in a deep crucible may be made to give a little lower results than slow heating in a shallow dish with such a coal as No. 12 (brown coal), but with coal No. 11 (jet) it was necessary to heat very slowly, even in a dish, so as to avoid too great a heat, which might allow dry distillation of combined sulphur without complete oxidation.

Hundeshagen's loss, which he attributed to the inability of sodium carbonate to retain all the sulphur of brown coals, may be due to rapid heating in a crucible of the sodium carbonate mixture, which is also more dusty than one of coal, magnesia, and potassium carbonate.

3. The "sintering" methods, when performed with good

judgment, agree closely with the results obtained by fusion of the coal with sodium carbonate and potassium nitrate.

4. If the "fusion method" is used, or sodium peroxide employed as an oxidizing agent, great care must be taken to dehydrate all silica by evaporation with hydrochloric acid.

Some chemists direct that the fused mass should be boiled with water and filtered before acidification with hydrochloric acid.[1] Other authorities state that the fused mass is to be dissolved directly in dilute acid.

The first procedure is to be preferred as the iron oxide and insoluble matters are removed at once by the filtration of an aqueous solution of the fusion.

5. The purest and most efficient reagent to complete the oxidation of sulphur compounds in the aqueous solution of the ignited residue of the "ignition" methods is a saturated solution of bromine in water. The use of hydrogen peroxide involves the testing of every bottle of the reagent for the very variable quantity of sulphuric acid it always contains. If this impurity is determined by a blank analysis and the amount deducted in the proper manner, the results obtained by its use are quite satisfactory (see 1, 3, 4, 12).

If sodium peroxide is added at first to a mixture of coal and magnesium oxide, the action is too violent. If added when the coal is nearly burned, the mass, nevertheless, balls on heating and some soluble sodium silicate appears to be formed by the heating or during subsequent aqueous extraction, and the barium sulphate will be a little impure unless silica is dehydrated by evaporation. Refer to coal analysis No. 7 (*c*) and (*d*).

In the writer's experience, no reagent gives as good results as the bromine water.

6. The five minutes' boiling of the ignited residue of coal ash, magnesium oxide, and carbonates with water (as generally prescribed by the authors) is sufficient to convert all the insoluble sulphates of lime, iron, etc., unless these substances are present in considerable quantity, or unless the magnesium oxide is a compact, heavy sample, as employed with No. 8B and No. 12. Under these circumstances the boiling and extraction of the ignited residue with water should be prolonged

[1] Blair's Iron Analysis; see also Stillman's Engineering Chemistry, p. 20.

for, say, an additional period of ten minutes—a precaution not alluded to by chemical authors, but a necessary one.

The two following experiments were made in order to show that this precaution must be taken with fuels, especially weathered coals, carrying a large amount of either iron or calcium sulphates.

TABLE III.

Sample No. 13.	Barium sulphate. Gram.
Taken, 1+ grams coal, yielding	0.0295
Added 0.1869 gram C. P. calcium sulphate, yielding	0.3202
Total	0.3507
Result of ignition, boiling five minutes with 100 cc. water + 15 cc. bromine and washing (blank allowed for)	0.2615
Deficiency =	0.0882

Sample No. 14.	Barium sulphate. Gram.
Taken, 1+ grams coal, yielding	0.0325
Added 0.4070 gram weathered ferrous sulphate containing the equivalent of	0.3490
Total	0.3815
Result of ignition, boiling five minutes with 100 cc. water + 15 cc. bromine and washing (blank allowed for)	0.3509
Deficiency =	0.0306

As far as my experience goes, the methods, irrespectively of Eschka and Hundeshagen, which involve a simple ignition, at low temperature, with a sulphur absorbent, are far preferable as rapid operations, suitable for technical work, to any plan necessitating a complete fusion with a consequent solution of silica. The two preferred methods will uniformly furnish accurate results, within usual limits of error in sampling, if the operator will only exercise a little judgment in certain cases.

With anthracite coal and coke there is no liability to error. With softer fuels, especially lignites, the materials should be especially well ground, well mixed, and stirred during the ignition in an open dish and if the proximate analysis and the appearance of the ash, indicates that the coal contains a large percentage (over three per cent.) of sulphur as pyrites (or calcium sulphate in the ash), the boiling and washing should be continued for a longer time, and the washed residue finally dissolved in acid, and qualitatively tested by itself.

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